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Ocean Acidification: The Newest Threat to the Global Environment

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Ocean acidification is the newest global environmental threat confronting the earth. It is the consequence of the same anthropogenic excess that is responsible for global warming—release of much more CO₂ at much faster rates, minute after minute, than the earth's capability to assimilate. Considering that oceans cover almost 70% of the earth's surface, any upset in the balance of forces in the oceans due to anthropogenic CO₂ emissions has, potentially, much more massive consequences than the impacts scientists are witnessing on the rest 30% of the earth. Ocean acidification is the name given to the lowering of ocean pH that is beginning to occur because the oceans are being forced to absorb CO₂ at a much faster rate during the last few decades than it has been over the previous thousands of years. The term does not imply that the oceans have actually become acidic, or will become acidic in the near future; it signifies a shift of ocean pH toward less alkaline levels. This shift has already threatened coral reefs and calcifying organisms. The latest forecast based on the most sophisticated models and the most authentic field data indicate that the adverse impact may become precipitous in the much more immediate future than was forecast previously. Ocean acidification has also come to be called the other CO₂ problem. Oceans are also absorbing large quantities of two more acid-forming gases being released at unprecedented rates into atmosphere—SO_x and NO_x. Thus far, on a global scale, their impact has been relatively minor; less than 3% of the impact

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of CO₂, but is expected to grow in magnitude as the emissions continue to increase. Moreover, the impact is likely to be much stronger in coastal regions, with serious portents for humankind.

KEY WORDS: aragonite saturation, calcification, corals, climate change, ocean acidification

1. INTRODUCTION

About 70% of the earth is covered by oceans. The enormous quantity of water contained in the oceans plays major roles in regulating the earth's temperature and other aspects of its climate, driving the gigantic hydrological cycle, providing habitat for thousands of genera of organisms, and performing a myriad other functions that strongly influence life on earth.

Among numerous other roles that the oceans play, one of the most important is the exchange of carbon dioxide with the atmosphere, thereby maintaining the earth's carbon cycle in a manner that preserves the ecological balance of the earth and enables a large number of life forms to thrive. This exchange of carbon dioxide with the atmosphere involves, on one hand, dissolution of carbon dioxide from the air into the ocean waters and, on the other hand, the release of carbon dioxide from the ocean to the atmosphere. A complex web of interactions control this exchange and, in turn, are controlled by the exchange (Figure 1). The details of the chemical and biological processes associated with this exchange are presented later in this paper. Had the exchange continued to occur as it has done in the past 800 thousands years, the average ocean pH would have remained about 8.2. But from 1950 onward, CO₂ emissions have started to rise steeply due to increased use of fossil fuels, cement production, agriculture, and various forms of land use changes (Doney, 2006). The rate of rise in CO₂ emissions is about 1% per year and is the prime reason for the global warming. But about a third of all the extra CO₂ emissions is being absorbed by the oceans. It is this CO₂ uptake, forced by excessive CO₂ emissions due to anthropogenic factors, that is causing the balance of ocean chemistry to shift, releasing more H⁺ than before. In turn this is causing a shift of the ocean pH toward less alkaline (hence more acidic) levels. Already the dissolution of CO₂ has lowered the average pH of the oceans by about 0.11 units from the preindustrial levels (Kleypas et al., 2006; Raven et al., 2005).

The figure of 0.1 pH units may appear to be denoting an insignificant change but such is not the case. This is because pH is measured on a logarithmic scale, and a change of 0.1 units represents a whopping 30% increase in the concentration of hydrogen ions in the oceans. With the increase in anthropogenic release of CO₂ into the atmosphere continuing

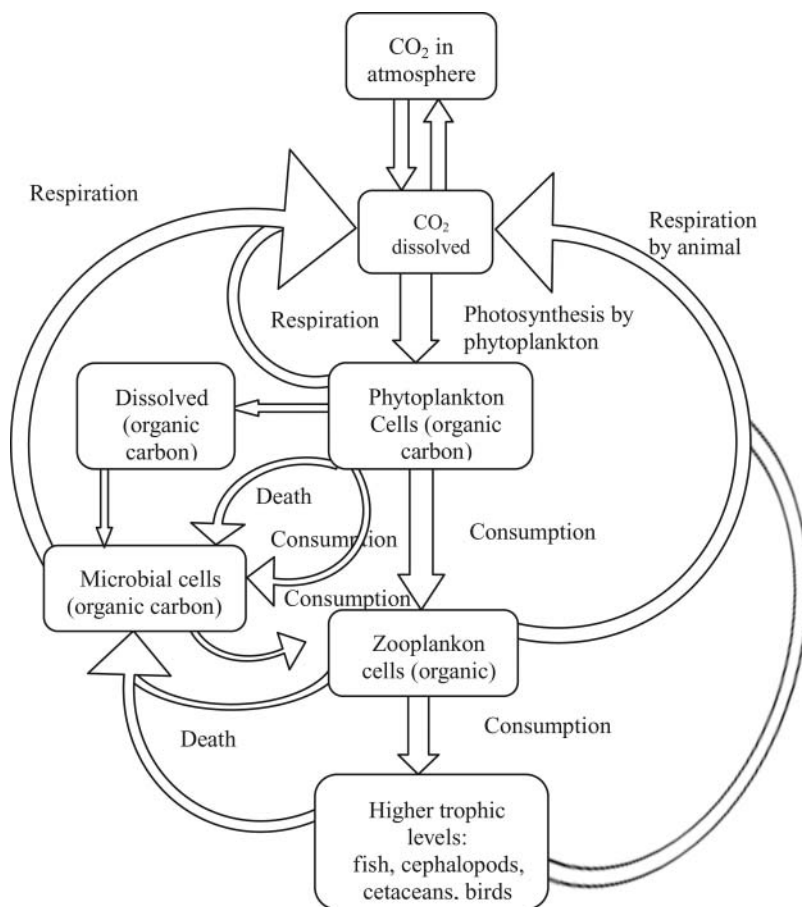


FIGURE 1. The complex web of interactions associated with the CO₂ cycle in the ocean (adopted from Raven et al., 2005).

unabated, the hydrogen ion concentration will further increase and may double the present excess soon. By the end of this century the pH is projected to drop another 0.3–0.4 pH units (Caldeira et al., 2007; Feely et al., 2008). This translates to a 100–150% increase in $[H^+]$. Ocean acidification of this magnitude probably has not occurred for more than 20 million years of the earth's history (Doney et al., 2009; Feely et al., 2004).

Alongside lowering the ocean pH, an increase in the concentration of CO₂ in the atmosphere causes an increase in the dissolved CO₂ levels in the oceans, and an increase in bicarbonate ion concentrations, with a concomitant reduction in the concentration of carbonate ions. Large changes may also occur in total alkalinity (Ilyina et al., 2009). All these changes have very ominous portents for the ocean's environmental balance.

The oceans are currently taking up about one ton of CO₂ associated with human activities per year for each person on the planet (Intergovernmental Panel on Climate Change [IPCC], 2001, 2007). Almost half of the CO₂ produced in the past 200 years by burning fossil fuels and cement manufacture has already been absorbed by the oceans (Raven et al., 2005). As more CO₂ enters the atmosphere from human activity, more is taken up by the oceans (Table 1). If CO₂ emissions continue on present trends, this could result in the average pH of the surface of the oceans decreasing by 0.5 units below the level in preindustrial times, by the year 2100. This is beyond the range of fluctuations in the oceanic pH that occur naturally and represents a level probably not experienced for at least 800,000 years and possibly much longer (Caldeira and Wickett, 2003; Lüthi et al., 2008). The rate of change is also at least 100 times higher than the maximum rate observed during this time period (Meehl et al., 2007; Siegenthaler et al., 2005). As these changes are occurring rapidly (compared to natural changes that occur very slowly over a time scale of thousands of years), they significantly reduce the buffering capacity of the natural processes that have moderated changes in ocean chemistry over most of geological time. Anthropogenic emissions of CO₂ and other greenhouse gases are also causing global averaged increase in temperature of 0.2°C per decade (IPCC, 2007). There is increasing evidence that adverse effects of global warming on marine ecosystems operate in synergy with the adverse effects of ocean acidification, thereby magnifying both (Byrne et al., 2009; O'Donnell et al., 2009; Parker et al., 2009).

Concerns have been expressed recently (Doney et al., 2009; Doney et al., 2007) that higher than natural emissions of nitrogen and sulfur oxides during postindustrial years is also contributing to ocean acidification and that even as their impact may be minor thus far, it may become increasingly significant in years to come.

Ocean acidification is very likely to cause the Southern Ocean to become undersaturated with respect to aragonite in the near future. This would lead to severe consequences for organisms that make the aragonite form of CaCO₃ shells and plates (Orr et al., 2005). Tyrrell et al.'s (2007) and Feely et al.'s (2008) observations of seasonal aragonite undersaturation of surface waters in temperate, near shore regions, field studies done elsewhere (Bernhard et al., 2009; Hall-Spencer and Rodolfo-Metalpa, 2009) combined with historical evidence (Wei et al., 2009) suggest that some calcareous organisms may already be experiencing substantial, transient changes in seawater CO₂ chemistry. A comparison of shell weights of the foraminifer *Globigerina bulloides* collected from sediment traps in the Southern Ocean with the weights of shells preserved in the underlying Holocene-aged sediments, by Moy et al. (2009), revealed that modern shell weights are 30–35% lower than those from the ancient sediments. This is consistent with the expectation that reduced calcification is now occurring due to ocean acidification. The authors also found a link between higher atmospheric CO₂ and low shell

TABLE 1. Forecasts of atmospheric CO₂ concentrations and their impact on the ocean chemistry

Aspect	Glacial	Preindustrial	Today	2 × preindustrial	3 × preindustrial	4 × preindustrial	5 × preindustrial	6 × preindustrial
Atmospheric concentration of CO ₂	180	280 ppm	380 ppm	560 ppm	840 ppm	1120 ppm	1400 ppm	1680 ppm
H ₂ CO ₃ (mol/kg)	7	9	13	19	28	38	47	56
HCO ₃ ⁻ (mol/kg)	1666	1768	1867	1976	2070	2123	2160	2183
CO ₃ ²⁻ (mol/kg)	279	225	185	141	103	81	67	57
Total dissolved inorganic carbon (mol/kg)	1982	2003	2065	2136	2201	2242	2272	2296
Average pH of surface oceans	8.32	8.18	8.07	7.92	7.77	7.65	7.56	7.49
Hydrogen ion (H ⁺) (μmol/kg)	4.79 × 10 ⁻³	6.92 × 10 ⁻³	8.92 × 10 ⁻³	12.3 × 10 ⁻³	17.4 × 10 ⁻³	—	—	—
Calcite saturation	6.6	5.3	4.4	3.3	2.4	1.9	1.6	1.3
Aragonite saturation	4.3	3.4	2.8	2.1	1.6	1.2	1.0	0.9
Temperature (°C)	15.7	19	19.7	20.7	22.7	—	—	—
Salinity (ppt)	35.5	34.5	34.5	34.5	34.5	—	—	—

weights in a 50,000-year-long record obtained from a Southern Ocean marine sediment core. In another study (De'ath et al. 2009), cored from several hundred massive *Porites* colonies on the Great Barrier Reef, which evinced a 14% reduction in calcification since 1990, an unprecedented event in at least the last 400 years that reflects warming and acidification.

Seasonal acidification is also in evidence as water with aragonite saturation rate less than 1 (indicating undersaturated or corrosive conditions) upwells along the California coastline in summer, decades earlier than models had predicted (Feely et al., 2008). Also, some high-latitude polar and subpolar waters may see similar situation by midcentury or earlier (Orr et al., 2005; Steinacher et al., 2009). More worrisome is the realization that the forecasts of ocean acidification made hitherto may even be somewhat conservative because fossil fuel CO₂ emissions in recent years have exceeded those predicted by the most extreme scenario from the 1990s (Raupach et al., 2007). This implies that future atmospheric CO₂ levels may exceed present model predictions, and the oceans may acidify much faster and more severely than hitherto forecast.

Hence, it can be said that adverse impacts of ocean acidification have begun to manifest in no uncertain terms. By all indications, ocean acidification has set in motion major destabilizing processes, the impact of which is likely to show up in ways that are not yet fully anticipated.

2. CO₂ AND THE BALANCE OF EARTH'S ECOSYSTEM

Alongside oxygen, CO₂ is the most important of gases in the atmosphere vis a vis day-to-day maintenance of life on Earth. CO₂ provides a major source of carbon to plants for photosynthesis (Abbasi and Abbasi, 2010a), maintains the earth's temperature pattern (radiative balance), and controls the calcium carbonate (CaCO₃) equilibrium in the oceans. The last of the three roles is crucial to the survival and growth of corals and other calcifying organisms, in turn, of the balance of the entire ocean ecosystem (Abbasi and Abbasi, 2011a; Hoegh-Guldberg, 2009; Munday et al., 2009).

The carbon from carbon dioxide that is taken up by the plants during photosynthesis to form biomass, and the carbon that is absorbed by oceans in the form of CO₂, constitutes major portions of the earth's carbon reservoir. From these reservoirs carbon is put back in the atmosphere as CO₂ is released by respiration, including the CO₂ released by microbial respiration when dead plants and animals are degraded by aerobes. Lesser quantities of carbon are also returned in the form of CO₂–CH₄ mixtures generated during anaerobic degradation of phytomass (Abbasi and Abbasi, 2010b).

For 800,000 years prior to the Industrial Revolution, atmospheric CO₂ concentrations remained between 180 and 300 parts per million by volume (ppmv; Augustin et al., 2004; Lüthi et al., 2008; Petit et al., 1999; Siegenthaler

et al., 2005). Increased fossil fuel burning associated with industrialization, cement production, and land use changes associated with agricultural activities have then caused atmospheric CO₂ concentrations to rise, and at increasing rates. For example, the rates of increase rose from 0.25% y⁻¹ in the 1960s to 0.75% y⁻¹ in the last five years. The present atmospheric CO₂ concentration is about 380 ppmv and is expected to continue to rise by about 1% y⁻¹ over the next few decades (Houghton, 2001; Kleypas et al., 2006; Raven et al., 2005). The rate of present and projected CO₂ increase is about 100 times faster than has occurred over the past 800,000 years (Doney et al., 2009). Moreover the rising atmospheric CO₂ levels will not be reversible on human timescales (i.e., a few centuries).

Across the 1980s and 1990s, only about half of the CO₂ released by human activity has remained in the atmosphere, with the oceans having taken up about 30% and the terrestrial biosphere 20% (Sabine et al., 2004). Similar dissolution of anthropogenic CO₂ by the oceans is expected to continue, with the result that the partial pressure of CO₂ (pCO₂) dissolved in the surface ocean is likely to double its preindustrial value within the next 50 years. Over the next millennium, the ocean will absorb about 90% of the anthropogenic CO₂ released to the atmosphere (Archer et al., 1998; Berelson et al., 2007; Fabry et al., 2008). Even in the entirely improbable scenario wherein all further anthropogenic greenhouse gas emissions are totally stopped forthwith, ocean acidification will persist for centuries due to the time scales associated with climate processes and feedbacks (IPCC, 2007). Thermal expansion of oceans will also continue for many centuries, due to the time required to transport heat into the deep ocean.

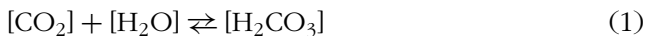
Tripling the preindustrial atmospheric CO₂ concentration will cause a reduction in surface ocean pH that is almost three times greater than that experienced during transitions from glacial to interglacial periods (Doney, 2009). This phenomena is termed *ocean acidification* because it describes the process of decreasing pH, but it must be clarified that ocean acidification does not mean oceans have become acidic, or will become acidic soon. The term implies that the oceans are becoming less basic, but not acidic. In fact oceans can become acidic (i.e., the oceanic pH may fall below 7.0) only in the unlikely event of CO₂ emissions reaching more than 11 times the present value (Caldeira and Wickett, 2005).

3. THE ROLE OF CO₂ IN THE OCEAN CHEMISTRY

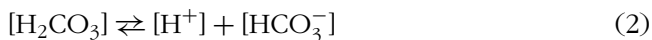
3.1 The pH, Calcium, Carbonate, Bicarbonate System

As CO₂ dissolves in seawater, a part of it reacts with the water molecule (H₂O) to form carbonic acid (H₂CO₃), and the rest remains as dissolved

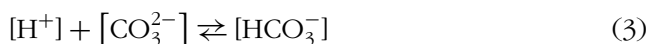
gaseous CO₂.



Carbonic acid dissociates to bicarbonate and hydrogen ions:

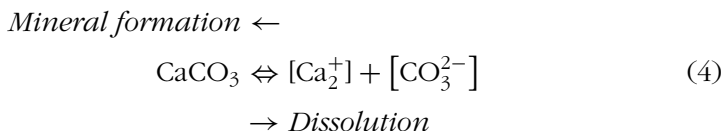


This increase in H⁺ causes some CO₃²⁻ (carbonate ion) to react with H⁺ to become HCO₃⁻



Thus, the net effect of the dissolution of CO₂ in seawater is to increase concentrations of H⁺, H₂CO₃ and HCO₃⁻, while decreasing the concentration of CO₃²⁻.

As mentioned previously, the decrease in carbonate ion concentration [CO₃²⁻] has important consequences for the chemistry of carbonate minerals commonly used by marine biota (plankton, corals and coralline algae, and many other invertebrates) to form shells or skeletons. The formation and dissolution of carbonate minerals can be represented as:



Because the dissolution of CO₂ in seawater decreases the [CO₃²⁻], the above reaction moves to the right, impeding the formation of carbonate minerals and promoting their dissolution. The dissolution of carbonate minerals provides carbonate ions that can react to consume H⁺ according to Equation 3. Thus, the dissolution of carbonate minerals would occur to decrease [H⁺] (increase pH), thereby counteracting some of the H⁺ generating effects of added CO₂ (Morse et al., 2007).

In summary, CO₂ dissolved in seawater exists in four main inorganic forms collectively known as dissolved inorganic carbon (DIC). These are (a) aqueous CO₂ and carbonic acid (H₂CO₃; about 1% of the total), (b) bicarbonate (HCO₃⁻; about 91%), and (c) carbonate ions (CO₃²⁻; about 8%). Thus, under present ocean conditions, bicarbonate is the most abundant form of CO₂ dissolved in seawater, followed by carbonate and then aqueous CO₂ (Figure 2). There is approximately an order of magnitude difference in abundance between each of the three forms; though the amounts vary somewhat with seawater temperature, salinity, and pressure.

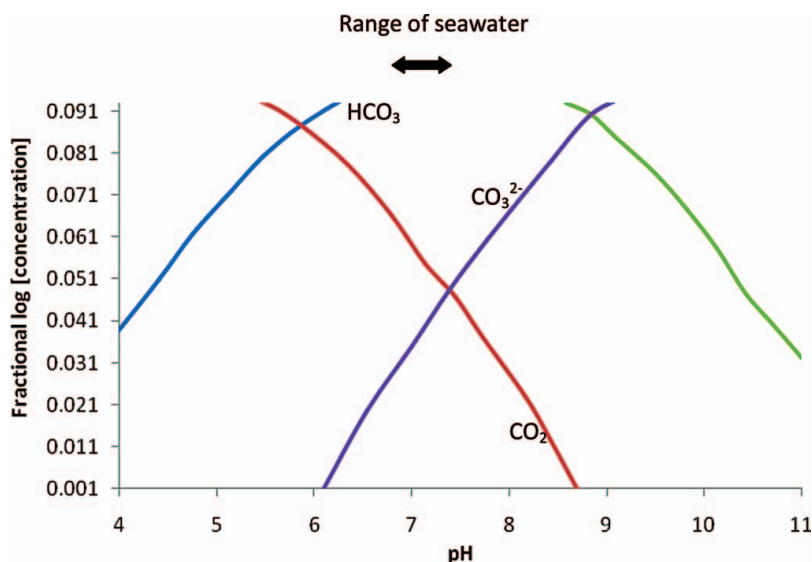


FIGURE 2. pH-based distribution of dissolved CO_2 , bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) in seawater (Color figure available online).

3.2 Aragonite and Calcite Saturation Rates

CaCO_3 formation and dissolution rates vary with the saturation state, Ω , of its mineral forms—calcite and aragonite—defined as the ionic product of calcium and carbonate ion concentrations:

$$\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{sp}$$

The apparent solubility product, K_{sp} , depends on temperature, salinity, pressure, and the type of mineral phase; aragonite is approximately 50% more soluble than calcite (Mucci, 1983). Shell and skeleton formation generally occurs where $\Omega > 1.0$. The dissolution occurs where $\Omega < 1.0$, unless the shells or skeletons are protected by organic coatings.

The solubility of CaCO_3 increases with decreasing temperature and increasing pressure. Hence saturation states are highest in shallow, warm tropical waters and lowest in cold, high-latitude regions. Saturation rates also decrease with depth. As a consequence, the aragonite and calcite saturation horizons ($\Omega = 1$) are shallower in the Indian and Pacific Oceans than in the Atlantic Ocean because of the longer deep-water circulation pathways and thus accumulation of more DIC from respired CO_2 (Broecker, 2003; Doney et al., 2009).

Anthropogenic CO_2 penetration into the ocean is largely confined to the upper thermocline (Sabine et al., 2004). Due to resultant hastening of CaCO_3 dissolution this has led to a reduction in the depths of the CaCO_3 saturation zones by 30–200 m from the preindustrial period to the present. This is also

the reason behind aragonite undersaturation in thermocline waters in the North Pacific and Indian Oceans (Feely et al., 2002; Sabine et al., 2002). The seasonal upwelling of seawater corrosive to aragonite ($\Omega_{\text{arag}} < 1.0$) is occurring in the western continental shelf of North America, approximately 40 years earlier than predicted by models (Feely et al., 2008); and an increase in areal extent of shallow under saturated regions in the eastern tropical Atlantic (Chung et al., 2003; Chung et al., 2004) have also been caused by the dissolution of anthropogenic CO_2 into the upper thermocline of the oceans.

3.3 Roles of Alkalinity and DIC

Another factor that influences the ocean chemistry is total alkalinity (A_t). A_t denotes the concentration of all the bases that can accept H^+ when a titration is made with HCl to the carbonic acid endpoint (Abbasi, 1998; Raven et al., 2005). Processes that increase DIC (e.g., adding CO_2 to the water column) shift the equilibrium toward lower pH and lower CO_3^{2-} concentration, while processes that increase A_t (e.g., the dissolution of calcium carbonates) shift the equilibrium toward higher pH and higher CO_3^{2-} concentration. Photosynthesis and respiration primarily affect DIC, while calcification and dissolution (Figure 3) affect DIC and A_t .

All the forms of DIC are important for the biological processes of marine organisms. These processes include photosynthesis by marine algae and other phytoplankton, the production of complex organic carbon molecules from sunlight, and calcification (providing CaCO_3 based body parts and

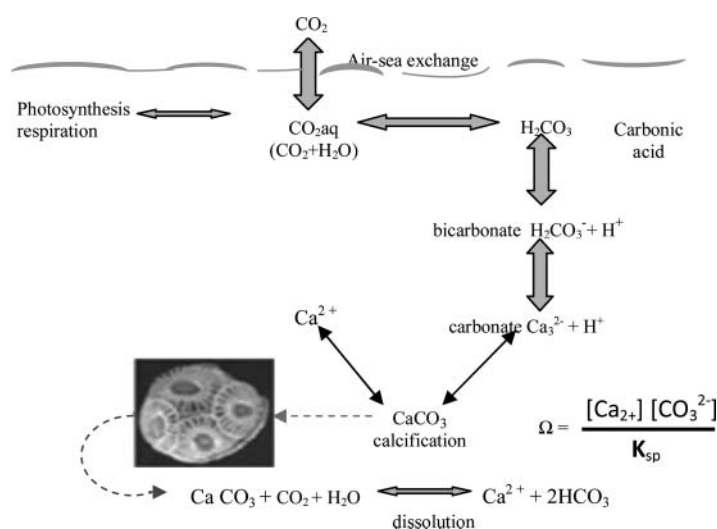


FIGURE 3. Oceanic processes that effect dissolved organic carbon (DIC) and total alkalinity (A_t) in oceans (adopted from Kleypas et al., 2006)

structures). Calcification draws down A_t twice as fast as it draws down DIC, and thus leads to a decrease in pH, which decreases the capacity of the upper ocean to take up atmospheric CO_2 (Kleypas et al., 2006; Raven et al., 2005).

When the oceanic organisms die or are consumed, most of the carbon either stays in the surface waters or is released back into the atmosphere. However, some of this CaCO_3 and organic material sediments down as particles to the ocean depths. The process whereby carbon is transferred from the atmosphere to the deep ocean waters and sediments is referred to as the *biological pump*. By removing carbon from the surface waters and taking it to greater depths, the pump increases the capacity for the oceans to act as a sink for atmospheric CO_2 . Any changes in the strength of this pump would have significant consequences on the amount of carbon being sequestered to the deep ocean environments and therefore removed from the atmosphere.

3.4 Contributions From Nitrogen and Sulfur Oxides

During the postindustrial years, fossil fuel combustion and biomass burning fluxes of NO_x have gradually exceeded the natural fluxes from land to the atmosphere (IPCC, 2001). Human activities, mainly livestock husbandry, has released much more NH_3 than natural emissions and oxidized sulfur fluxes from land are as much as 10 times the natural fluxes, because of combustion of fossil fuels and biomass burning.

After chemical transformations in the atmosphere, much of the anthropogenic nitrogen and sulfur is deposited to the ocean and land surface in the form of nitric acid (HNO_3) and sulfuric acid (H_2SO_4), which are strong acids that completely dissociate in water:

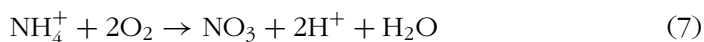


Because of the relatively short lifetime of reactive nitrogen and sulfur species in the atmosphere (days to about a week), the majority of the acid deposition occurs on land, in the coastal ocean, and in the open ocean downwind of the primary source regions: North America, Europe, and South and East Asia (Dentener et al., 2006; Rodhe et al., 2002). The subsequent acidification of terrestrial and freshwater ecosystems by dry deposition and more acidic rainfall is a well known environmental problem (Abbasi and Soni, 1983, 1984; Khan and Abbasi, 1997a, 1997b, 1998a, 1998b, 2000, 2001).

Most of the atmospheric sulfur is oxidized to H_2SO_4 by gas-phase and aqueous reactions and deposited to the surface by wet (dominant) and dry processes. An input of 1 mole SO_4^{2-} is equivalent to a reduction of $\pm \sim 2$

equivalents of ocean water alkalinity. The remaining sulfur emissions are dry-deposited as SO_2 .

Atmospheric nitrogen deposition can add either acidity or alkalinity, depending on the chemical form. The wet deposition of NO_3^- is acidic while the impact of atmospheric $\text{NH}_4^+ + \text{NH}_3$ input on ocean alkalinity depends on the extent to which the NH_4^+ is converted to NO_3^- by nitrification:



This reduces the alkalinity by 2 equivalents for every mole of NH_4 consumed.

Of the total anthropogenic NO_x and SO_x emissions, about one third are deposited to the ocean. As the deposition is concentrated downwind of the emission sources, it impacts mostly the temperate North Atlantic, temperate and eastern subtropical North Pacific, and northern Indian Ocean, with maximum values approaching $\sim 0.03 \text{ mol m}^{-2} \text{ y}^{-1}$. Approximately half of agricultural NH_x emissions are deposited in the oceans and are more evenly spread over the Northern Hemisphere (Doney et al., 2007). This flux will increase significantly during the next several decades, as will the reactive nitrogen flux to the coastal ocean from anthropogenic sources via rivers and groundwaters. Globally, the ocean acidification due to anthropogenic sulfur and nitrogen deposition at present is under $\pm 3\%$ of the contribution of CO_2 uptake (Doney et al., 2009). However, the impacts can be significant in some coastal ocean and margin areas of the order of 10–50% or more of the anthropogenic CO_2 -driven changes near the major source regions and in marginal seas. Moreover, the extent of atmospheric neutralization of acidic compounds may vary due to the changes in mineral dust and alkaline fly ash emissions from coal-fired power plants. There is evidence, for example (Hedin et al., 1994) of reduced atmospheric deposition of basic cations (e.g., Ca^{2+}).

Of the acidity flux that falls on land, much is neutralized by soils (Abbasi et al., 2011), but some fraction may be transported to the ocean (Galloway, 2003). There are also substantial riverine inputs of anthropogenic nitrogen and organic matter to the coastal domain (Galloway et al., 2004). The contributions of wastewater inflows are also significant (Abbasi and Abbasi, 2009; Reopanichkul et al., 2009). The cumulative impact of all these inputs on the ocean acidification may be quite high, surely in regions where multiple inputs occur (Keller et al., 2009).

3.5 Consequence of Very Slow Vertical Mixing in Oceans

It must be highlighted here that the impact of ocean acidification is not only very strong in near surface waters, but also that the effect is transmitted downward very slowly. It may take several hundred years for the impact to reach the deeper ocean waters. This is because CO_2 enters the oceans

by exchange across the air–sea interface, hence distribution of CO₂ uptake show highest values (and therefore the greatest pH change), in near-surface waters. As it takes many centuries for the downward mixing of CO₂, little of the CO₂ derived from human activities has yet reached the deep oceans. When averaged for the oceans globally, about 30% of the anthropogenic CO₂ is found at depths shallower than 200 m and 50% at depths less than 400 m. This has led to the conclusion that most of the CO₂ that has entered the oceans as a result of human activity still resides in relatively shallow waters. As is elaborated later, this situation has a strong role in enhancing the harmful effect of ocean acidification on the marine biota.

Even as CaCO₃ dissolution is substantial in the upper water column, little is known about the mechanisms that control this dissolution or how they may change with increased CO₂ in future. Indeed, the CO₂ dissolution rates are unexpectedly high in the upper ocean, even in supersaturated waters. It is estimated that up to 70% of the calcite and aragonite dissolves before it reaches the pycnocline (Feely et al., 2002; Feely et al., 2004; Milliman et al., 1999), and process studies in the equatorial Pacific and Arabian Sea suggest that 75–80% of the calcite flux dissolves in the upper 800–900 m of water (Balch et al., 2000; Balch and Kilpatrick, 1996). Several mechanisms for these high dissolution rates have been proposed but none has been adequately quantified or tested. Microbial processes (Schiebel, 2002; Troy et al., 1997) and dissolution in acidic zooplankton guts (Bishop et al., 1980; Harris, 1994; Pond et al., 1995) are possibly involved. An improved understanding of these processes is needed to predict how upper ocean dissolution rates will change with increased ocean acidification.

It has been estimated that between the years 1800 and 1994 the oceans absorbed about 48% of the total CO₂ emitted by human activities, mainly by fossil fuel burning and cement manufacturing. This was deduced from the measurement of total DIC (106 ± 17 Gt C) and extrapolating for the regions of oceans not surveyed, leading to a sum of 118 ± 19 Gt C over this period. A continuation of trends inferred for the 1980s and 1990s from ocean models and atmospheric observations would indicate that over 140 Gt C (over 500 Gt CO₂) resulting from human activities resides in the oceans today.

4. IMPACT OF THE HIGH ATMOSPHERIC CO₂ CONCENTRATIONS, AND DISSOLUTION OF LARGE FRACTION OF THE EXCESS EMISSIONS BY OCEANS, ON THE OCEANS' BUFFERING CAPACITY

When the phenomena of ocean acidification was initially detected, a section of scientists tended to dismiss it as of no consequence, saying that the ocean's natural buffering capacity would soon neutralize the extra hydrogen ions

(Abbasi et al., 2000). Indeed the same argument was given to dismiss even global warming as a short-term transient phenomena, arguing that oceans would soon absorb all the excess CO_2 and the gigantic buffering ability of the oceans would then assimilate the excess CO_2 without any perceptible long-term harm to anything.

Unfortunately, neither the solution to the problem of global warming, nor the solution to the problem of ocean acidification, is that easy. In fact, the world is becoming painfully aware that these threats are much more difficult to repel than other environmental threats faced, such as of epidemics caused by polluted water or municipal solid waste.

The ocean waters do have a strong buffer capacity that has in the past helped it in maintaining its pH even as it absorbed CO_2 and released it back as the normal CO_2 exchange process. The term *carbonate buffer* is used to describe how the dissolved inorganic carbon in seawater (in the forms discussed in Section 3.1) acts to diminish changes in ocean H^+ concentration, and thus prevents the pH from changing. When CO_2 dissolution (Equation 1), adds H^+ to seawater, some of the added H^+ reacts with carbonate (CO_3^{2-}) ion to convert it to bicarbonate (HCO_3^- ; Equation 3). Because initially most of the added H^+ would be consumed in this way, the change in pH is much less than it would be otherwise. But this process also consumes some carbonate ion; therefore, this pH buffering capacity would diminish as CO_2 concentrations increase.

The CaCO_3 -rich sediments of the oceans also contribute toward preventing the fall in pH but this process is much slower than the acidify-enhancing role of carbon dioxide. When the bottom layers of the oceans start becoming more acidic, due to the long-term impact of CO_2 , which decreases concentrations of CO_3^{2-} , some carbonate ions will be dissolved from sediments (Equation 5) and thereby counter the lowering of the pH. But it will take tens of thousands of years for ocean chemistry to return to a condition similar to that occurring at preindustrial times (i.e., about 200 years ago). The delay arises because it takes tens of thousands of years for mixing to take place throughout the oceans. This mixing is required to bring up compounds from the oceans' sediments to buffer the changes as a result of increased CO_2 on ocean surface chemistry. As we have highlighted previously, the oceans have in the past been able to adapt to increased atmospheric CO_2 levels because the rate of change took place over time periods of several thousand years that enabled sufficient mixing with deeper waters. The present pace of ocean acidification is essentially too hot to be reversible by the much slower counteracting natural mechanism during our lifetimes. To put it in other words, even though the ocean is capable of eventually absorbing all the excess CO_2 (which is causing global warming at present), as also eventually self-adjust its pH to its normal levels, these processes are so slow that no perceptible improvement in the situation is likely in this lifetime or even in the next few hundred years!

The carbonate buffer acts to stabilize the average pH of seawater at approximately pH 8 because of the following two processes: (a) uptake of CO₂ from the atmosphere (e.g., from volcanoes and now, also, from fossil fuel burning) and (b) interaction of seawater with oceanic sediments composed of CaCO₃.

5. FORECASTS OF FURTHER OCEAN ACIDIFICATION

What does this mean vis a vis ocean acidification? Several attempts have been made to estimate the extent of acidification that may occur.

The simplest estimate takes a situation where human CO₂ emissions continue to be released on present trends; considers the surface oceans as a single box at a constant temperature (25°C) and salinity, an initial (preindustrial) pH of 8.2 units, and assumes no mixing with the deeper oceans. Under these circumstances it is predicted that pH will fall to below 7.9 by 2100 (Zeebe and Wolf-Gladrow, 2001). A more detailed analysis of the projected pH changes has been done using an ocean general-circulation model with observed atmospheric CO₂ from 1975 to 2000 and a projected midrange CO₂ emission scenario (IPCC IS92a scenario; Houghton et al., 2001) for 2000–2100 (Caldeira and Wickett, 2003). The study predicted a possible decrease in pH of 0.5 units by the year 2100 in the surface oceans, which, as stated previously, corresponds to a threefold increase in the concentration of hydrogen ions from preindustrial times. The simulated atmospheric CO₂ exceeds 1900 ppm at around 2300, and the maximum reduction in pH in the oceans' surface would be 0.77 units. The lowering of pH would be moderated slightly by factors such as changes in temperature, but by less than 10%. Hence these changes in ocean pH are outside the range of natural variability and, as explained previously, could have a substantial effect on the biological processes in the surface oceans. The more recent forecast of the IPCC (2007) stated that even if radiative forcing were to be stabilized (e.g., by stopping further rise in anthropogenic greenhouse gas emissions and by geoengineering), a further reduction in average global ocean pH of between 0.14 and 0.35 units may still occur over the present century.

Another modeling exercise (Orr et al., 2005) indicated that in the cold high-latitude surface waters typical of the subarctic North Pacific and North Atlantic, and the Subantarctic and polar regions of the Southern Ocean, aragonite and calcite undersaturation occurs when pCO₂ reaches 600 and 900 μ atm, respectively (Figure 4). In the warm tropical and subtropical waters undersaturation occurs when pCO₂ values reach about 1700 and 2800 μ atm, respectively. If CO₂ emissions continue as projected, aragonite-undersaturated regions will develop in the Subarctic, Subantarctic, and polar surface waters by the end of the 21st century. This would occur first in the wintertime when surface water temperatures are coldest and pCO₂ values are highest due to

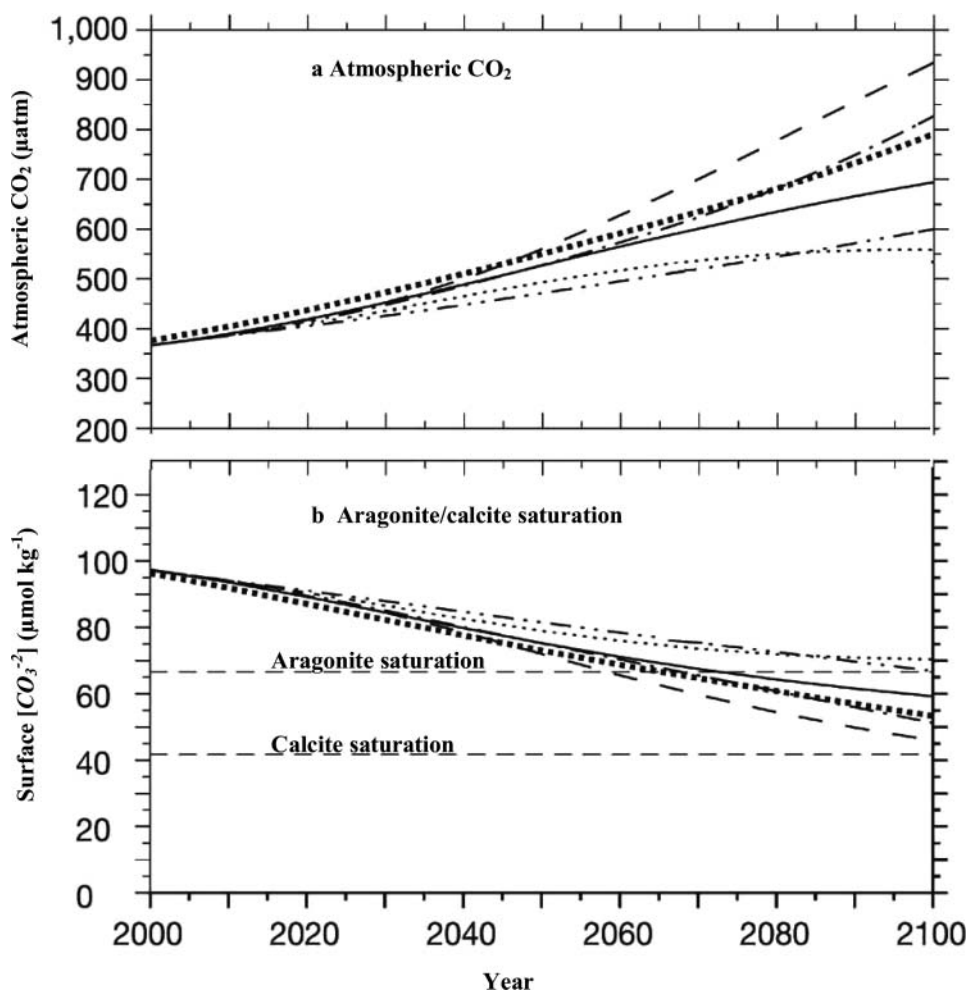


FIGURE 4. Illustrative model projections that (a) forecast rise in atmospheric CO₂ and (b) concomitant reduction in the aragonite/calcite saturation rates. Undersaturation is likely to occur by the middle of this century. Adopted from Orr et al. (2005). The quantification of future changes is based on simulated dissolved organic carbon according to the IPCC IS 92a and S650 scenarios which project 788 and 563 ppmv CO₂ respectively in the year 2100; alkalinity was assumed to be constant.

wind-driven mixing of subsurface waters into the mixed layer. Undersaturated regions would then expand toward the equator. The accuracy of these forecasts is already apparent; investigations have revealed that the aragonite and calcite saturation horizons are moving to shallower depths in the North Pacific at a rate of 1–2 m per year. Many of the areas where shoaling is predicted to occur within this century are highly productive and home to many of the world's most important and economically lucrative commercial

fisheries. Moreover, for any given atmospheric CO₂ scenario, changes in surface ocean CO₃²⁻ concentrations can be predicted with much more certainty than the related changes in climate.

Even though seawater carbon dioxide measurements have been conducted since the beginning of the nineteenth century (Krogh, 1904), they were few and far between until the early 1970s. This situation was remedied by Geochemical Section (GEOSEC; 1973–1979; Craig and Turekian, 1976, 1980) and Transient Tracers in the Ocean (TTO; 1981–1983; Brewer et al., 1985). Even so, the GEOSEC and TTO measurements were significantly less precise than those of today. Among numerous present initiatives to monitor the extent of CO₂ absorption by the oceans and its impacts is the British project CARBON-OPS (Hardman-Mountford et al., 2008). Under it, data is being gathered by new pCO₂ measurement systems on five UK research ships in the Southern Ocean, Atlantic Ocean, and northwestern European shelf seas. From these ships data is sent, in near-real-time, via satellite communication systems, to the British Oceanographic Data Centre where they are automatically processed, quality controlled, and archived. The data are then delivered to the UK Met Office and others for use in testing predictions from operational ocean models. These models will generate indicators and forecasts to assist the government through the Marine Climate Change Impact Partnership. This partnership connects scientists, government, its agencies, and NGOs, for utilizing information on ocean CO₂ uptake, changes in ocean pH, and the potential impacts.

A recent analysis (Dore et al., 2009) of time-series measurements of seawater pH and associated parameters at the Hawaii Ocean Time-Series (HOT) Station ALOHA, revealed a significant long-term decreasing trend in surface pH, which is indistinguishable from the rate of acidification expected from equilibration with the atmosphere. Superimposed on this trend was seen strong seasonal pH cycles driven by temperature, mixing, and net photosynthetic CO₂ assimilation. Substantial interannual variability was observed in surface pH, influenced by climate-induced fluctuations in upper ocean stability. Below the mixed layer, the change in acidification was seen to be enhanced within distinct subsurface strata. These zones were influenced by remote water mass formation and intrusion, biological carbon remineralization, or both. The studies revealed that physical and biogeochemical processes alter the acidification rate with depth and time and must therefore be given due consideration when designing and interpreting ocean pH monitoring efforts and predictive models.

In another recent study, changes in marine CaCO₃ production on total alkalinity (TA) in the ocean using the global biogeochemical ocean model HAMOCC were examined by Ilyina et al. (2009). They tested a variety of future calcification scenarios because experimental studies with different organisms have revealed a wide range of calcification sensitivities to the CaCO₃ saturation state. They conclude that the data presently available do

not allow discerning significant trends in TA due to changes in pelagic calcification caused by ocean acidification. Given different calcification scenarios, the model calculations indicate that the TA increase over time will start being detectable by the year 2040, increasing by 5–30/mol kg⁻¹ compared to the present-day values. The largest increase in surface ocean TA is predicted for the tropical and subtropical regions.

The Tyndall Centre for Climate Change Research at Manchester has been exploring how to downscale the global analysis of ocean acidification to the local level within the framework of a coastal simulator (Watkinson, 2009). The simulator provides information on possible future states of the coast through the 21st century under a range of climate and socioeconomic futures and shoreline management options. It links models within a nested framework, recognizing global, regional, and local scales. The linked models describe a range of processes, including marine climate (waves, surges, and mean sea level), sand bank morphodynamics, wave transformation, shoreline morphodynamics, built environment scenarios, ecosystem change, and erosion and flood risk. Analyses from the simulator reinforce conclusions from the IPCC forecasts (IPCC, 2007): coasts will be exposed to increasing risks over coming decades due to many compounding climate-change factors; the impact of climate change on coasts will be exacerbated by increasing human-induced pressures; and the unavoidability of sea-level rise even in the longer term frequently conflicts with present-day human development patterns and trends.

The most prevalent belief, as on date, is that ocean acidification together with the synergistic impacts of global warming and other anthropogenic stressors has the potential to cause widespread disturbances in the marine ecosystems (Byrne et al., 2009; Fabry et al., 2008; Parker et al., 2009). Moreover, even the nature of likely impacts, more so their magnitude, are largely shrouded in uncertainty (Todgham and Hofmann, 2009).

6. THE ORGANISMS MOST DIRECTLY AND SEVERELY ENDANGERED BY OCEAN ACIDIFICATION: THE CALCIFYING ORGANISMS

6.1 Calcifying Organisms and Calcification

The organisms likely to be affected the earliest and most strongly by ocean acidification are calcifying organisms. These include corals, mollusks, echinoderms, foraminifera, and calcareous algae (Table 2). These organisms depend on the formation of shells or plates of CaCO₃ in their bodies through a biological–chemical process commonly called *calcification*. This process is integral to their biology, so any decrease in calcification, as a result of increased CO₂, is therefore likely to have significant consequences such as the weakening of coral skeletons and reef structures generally. In other words,

TABLE 2. Major calcifying groups at risk from ocean acidification

Group	Trophic level	Mineral form	Generation time	Approximate number of species	Habitat
Coccolithophores	Autotrophic	Calcite	Day(s)	200	Planktonic
Coralline algae	Autotrophic	High-Mg calcite	Days	20 genera	Benthic or planktonic
Euthecosomatous pteropods	Heterotrophic	Aragonite	Several months	34	Planktonic
Foraminifera	Heterotrophic; many with autotrophic symbionts	Calcite	Weeks	35	Benthic
Halimeda	Autotrophic	Aragonite	Weeks	25–30	Benthic
Zooxanthellate corals	Heterotrophic with autotrophic symbionts	Aragonite	Months–years	1000	Benthic
Warm-water corals	Autotrophic	Aragonite	Months–years	~1000	Benthic
Crustaceans	Heterotrophic	Calcite	Days–months	>1000	Benthic or planktonic
Echinoderms	Heterotrophic	Calcite	Days–months	<1000	Benthic

calcifying organisms may not be able to generate and maintain their shells and plates as well as they are able to under normal circumstances. This may not only effect the survival and growth of these organisms but may have a cascading effect on numerous other organisms and the abiotic environment as a result of numerous imbalances that it may cause on the food chain and the bio-geo chemistry of the oceans (Doney et al., 2009; Fabry, 2008; Kleypas et al., 2006; Raven et al., 2005). Studies on the impact of increased $p\text{CO}_2$ on calcification of several organisms are summarized in Table 3.

Different constituents and niches in the oceanic ecosystems are strongly interactive and interdependent. For example, there is transport of alkalinity from shallow coral reef systems to the open ocean (Mackenzie et al., 2004; Sabine et al., 1995), between sea-grass beds and coral reefs (Burdige and Zimmerman, 2002), and in numerous other ways (Figure 5). Therefore even though stress on calcifying organisms is a near surface phenomenon, it would soon impact deep-sea biodiversity and ecology.

Whereas corals and a group of mollusks and pteropods precipitate aragonite; coccolithophores (calcifying phytoplankton) and foraminifera (protist plankton) produce the less soluble calcite, generally in internal compartments. Mollusk shells either consist of all aragonite or interlayered aragonite and calcite. Echinoderms, which include sea urchins, sea stars, and brittle stars, form calcite structures that are high in magnesium and have a very high porosity (often exceeding 50%). For these calcareous structures to form

TABLE 3. Impact of increased pCO₂ concentrations on calcification responses (adopted from Guinotte and Fabry, 2008; Kleypas et al., 2006)

Organism	Associated mineral	% change in calcification at pCO ₂		Reference
		2 × preindustrial	3 × preindustrial	
Coralline red algae <i>Porolithon gardineri</i>	Calcite	−25		Agegian, 1985
Coccolithophores <i>Emiliana huxleyi</i>	Calcite	−9	−18	Riebesell et al., 2000
<i>E. huxleyi</i>	Calcite	−25		Sciandra et al., 2003
<i>Gephyrocapsa oceanica</i>	Calcite	−29	−66	Zondervan et al., 2001
Foraminifera <i>Globigerinoides sacculifer</i>	Calcite	−4 to −6	−6 to −8	Bijma et al., 2002; Bijma et al., 1999
<i>Orbulina universa</i>	Calcite	−8	−14	Spero et al., 1997; Bijma et al., 1999
Mussel <i>M. edulis</i>	Calcite		−25 ^a	Fabry, 2008
Oyster <i>C. gigas</i>	Calcite		−10 ^a	Fabry, 2008
Scleractinian corals <i>Acropora cervicornis</i>	Aragonite	−40	−59	Renegar and Riegl, 2005
<i>Acropora eurystoma</i>	Aragonite	−55		Schneider and Erez, 2006
<i>Acropora verweyi</i>	Aragonite	−12	−18	Marubini et al., 2003
<i>Fungia</i> sp.	Aragonite	−47	−69	Hossain and Ohde, 2006
<i>Galaxea fascicularis</i>	Aragonite	−12	−18	Marubini et al., 2003
<i>G. fascicularis</i>	Aragonite	−56	−83	Marshall and Clode, 2002
<i>Porites compressa</i>	Aragonite	−17	−25	Marubini et al., 2001
<i>P. compressa</i> + <i>Montipora capitata</i>	Aragonite	−40	−59	Langdon and Atkinson, 2005
<i>Pavana cactus</i>	Aragonite	−14	−20	Marubini et al., 2003
<i>P. lutea</i>	Aragonite	−38	−56	Ohde and Hossain, 2004
<i>P. lutea</i>	Aragonite	−33	−49	Hossain and Ohde, 2006
<i>P. porites</i>	Aragonite	−16		Marubini and Thake, 1999
<i>Stylophora pistillata</i>	Aragonite	−14	−20	Gattuso et al., 1998
<i>S. pistillata</i>	Aragonite	0 to −50		Reymaud et al., 2003
<i>Turbinaria reniformis</i>	Aragonite	−9	−13	Marubini et al., 2003

^a2.6 × preindustrial.

properly, seawater has to be supersaturated with calcium (Ca²⁺) and carbonate (CO₃^{2−}) ions to ensure that once formed the CaCO₃ does not dissolve. Calcification is a delicately tuned biological process and prone to being upset unless the seawater is supersaturated with respect to CaCO₃. Lower pH would reduce the carbonate saturation of the seawater, making calcification harder and also weakening any structures that have been formed.

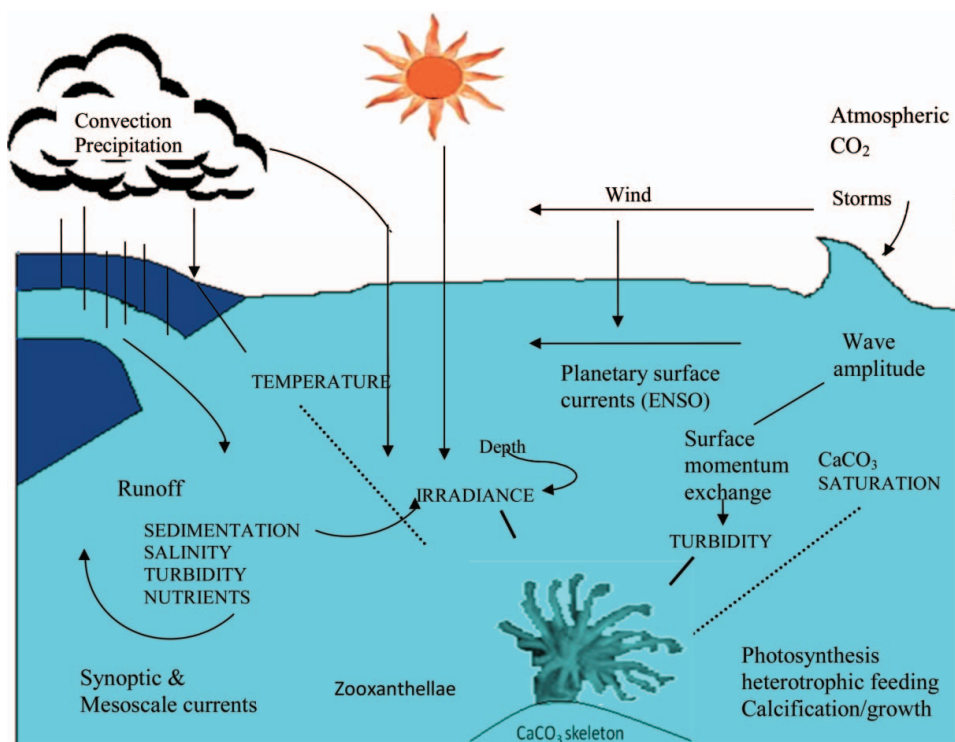


FIGURE 5. Interactions between energetic, hydrodynamic, chemical, and biological factors that influence calcification in corals (adopted from James and Crabbe, 2008) (Color figure available online).

Although calcite is less soluble than aragonite; making it less susceptible to pH changes; the incorporation of magnesium into either form increases their solubility and makes them also susceptible to lowered pH.

There is also evidence that dissolution rates of carbonates increase in response to CO₂ forcing (Table 4). Consequently, small changes in CO₂ concentrations in surface waters may have large negative impacts on marine calcifiers and natural biogeochemical cycles of the ocean (Gattuso et al., 1998; Langdon et al., 2000; Marubini et al., 2001; Reynaud et al., 2003; Riebesell et al., 2000; Wolf-Gladrow et al., 1999; Zondervan et al., 2001). This would not only affect individual corals but also the ability of the reef to maintain a positive balance between reef building and reef erosion (Kleypas et al., 2001).

Moreover, the response of calcifying organisms to CO₂-induced changes in seawater chemistry is not uniform and may be much more complex than previously thought (Egilsdottir et al., 2009; Iglesias-Rodríguez et al., 2008; Parker et al., 2009; Ries et al., 2008; Russell et al., 2009; Fabry, 2008). In the experiments conducted by Ries et al. (2008), the response of a variety

TABLE 4. Carbonate dissolution rates reported from reef environments and mesocosms (adopted from Kleypass et al., 2006)

Location	CaCO ₃ dissolution rate			Source
	mmol m ⁻² hr ⁻¹ at night	mmol m ⁻² night ⁻¹	mmol m ⁻² 24 hr ⁻¹	
One Tree Island, GBR back reef zone	3.0*			Kinsey, 1978
Rib Reef flat GBR in March	4.0		97.0	Barnes and Deveraux, 1984
Florida Bay	0.8		19.0	Walter and Burton, 1990
Reunion Island Back reef zone summer	7.0			Conand et al., 1997
Moorea sandy bottom reef flat and lagoon	0.8	9.4	2.4	Boucher et al., 1998
Biosphere 2 mesocosm*	0.2		4.7	Langdon et al., 2000
Monaco mesocosm*	0.8			Leclercq et al., 2002
Hawaiian patch reef 22% coral cover	1.5	17.7		Yates and Halley, 2003
Hawaiian patch reef 10% coral cover	1.1	13.0		Yates and Halley, 2003
Hawaiian coral rubble	1.2	14.1		Yates and Halley, 2003
Hawaiian sand bottom	0.3	3.3		Yates and Halley, 2003
Florida patch reef	0.5	5.5		Yates and Halley, 2003
Florida patch reef top	0.1	1.1		Yates and Halley, 2003
Florida seagrass	0.4	4.7		Yates and Halley, 2003
Florida sand bottom	0.3	3.0		Yates and Halley, 2003
<i>M</i> ± <i>SD</i>	2.3 ± 4.8	8.0 ± 5.5	42.6 ± 42.0	

Note. Projected calcification rates at future CO₂ levels for these mesocosms are given in Table 5.

of calcareous benthic invertebrates and macroalgae to a range of carbonate ion concentrations and aragonite saturation states was studied. Some organisms showed increased rates of calcification in response to elevated pCO₂, while others showed decreased calcification rates, and still others displayed a nonlinear, parabolic response as a function of carbonate saturation state. Even closely related organisms—for example, tropical and temperate sea urchins—showed different responses (Fabry, 2008). Embryonic development of the intertidal amphipod *Echinogammarus marinus* was hampered more by the lowering of salinity than by the pH (Egilsdottir et al., 2009). Direct exposure to carbon dioxide hydrate at water depths of >3 km did not impact the survival rates of agglutinated and thecate foraminifera but had a strong influence on the survivability of calcareous foraminifera (Bernhard et al., 2009). There is also mounting evidence that interactive effects of lowered pH with that of temperature, photosynthesis, species-specific sensitivities and adoptive responses, can be strong and complex, making impact forecasting exceedingly difficult (Gooding et al., 2009; Hall-Spencer and Rodolfo-Metalpa, 2009; Martin and Gattuso, 2008; McDonald et al., 2009;

Todgham and Hofmann, 2009; Widdicombe et al., 2009). These findings reemphasize the gigantic magnitude of the challenge associated with combating ocean acidification. On one hand the crisis is already looming large and on the other hand the global extent of knowledge on the nature of its likely impacts is not adequate to see properly even the proverbial tip of the iceberg.

6.2 Coral Reefs

An estimated 1.28 million square kilometers of the world's tropical and subtropical oceans are covered by coral reefs (Spalding et al., 2001). In the tropics, scleractinian corals and calcareous green and red algae are important to the building and cementation of the massive carbonate framework that forms the habitat for coral reef organisms (Table 2). In colder deep (50–1000 m) waters of the continental shelves and offshore canyons, deep-sea corals build carbonate thickets or groves of high complexity that provide habitat for many other organisms. It is the high rate of calcification that makes possible the development of scaffolding or framework in a coral reef, which becomes the habitat of hundreds of thousands of other species that dwell in coral reefs (Reaka-Kudla, 1996). Without the presence and activities of reef-building corals, coral reefs would not be the diverse and productive ecosystems that they are. The socioeconomic importance of coral reefs can be gauged from the fact that, though coral reefs cover less than 1.2% of the world's continental shelf area, they provide a critical resource base to people and industries in many countries (Spalding et al., 2001). In just one of the several coastal states of the United States, Florida, coral reefs create an annual income of over \$4 billion (Riegl et al., 2009).

The reefs in the warm-water regions of oceans generally exist within a narrow range of sea temperature, light and the aragonite saturation state (Kleypas et al., 1999a). The growth of coral reefs is minimal outside this range. Climate change, through its effect on ocean temperature and aragonite saturation state, has already had an impact on the world's coral reefs (Hoegh-Guldberg, 1999; Wei et al., 2009). Almost 30% of warm-water corals have disappeared since the beginning of the 1980s, a change brought about by global warming. High ocean temperatures cause corals to bleach (i.e., lose their pigmented dinoflagellate symbionts) and, if conditions remain unfavorable, to die. The increase in atmospheric CO₂ is compounding this effect by lowering the aragonite saturation state of seawater, making carbonate ions less available for calcification (Table 5). Gattuso et al. (1998) and Kleypas et al. (1999b) proposed that the calcification rates of corals would decrease by 10–30% under a doubling of atmospheric CO₂ concentrations. There is ample evidence now that coral calcification is directly proportional to the aragonite saturation (Gattuso et al., 1999; Langdon et al., 2003; Langdon et al., 2000; Leclercq et al., 2000, 2002; Marubini and Atkinson, 1999;

TABLE 5. Changes in calcification rates of mesocosms and reefs to increased $p\text{CO}_2$

Mesocosm/location	Associated mineral	% change in calcification at $p\text{CO}_2$		Reference
		2 × preindustrial	3 × preindustrial	
Bahamas bank	Mixed	−57	−85	Broecker and Takahashi, 1966
Biosphere 2	Mixed	−56	−83	Langdon et al., 2000
Monaco mesocosm	Mixed	−21		Leclercq et al., 2000
Monaco mesocosm	Mixed	−15		Leclercq et al., 2002
Nature reserve reef, Red Sea	Mixed	−55		Silverman et al., 2007
Rukan-sho, Okinawa	Mixed	−45	−67	Ohde and van Woesik 1999

Marubini et al., 2001; Marubini et al., 2002; Raven et al., 2005). A doubling in ambient CO_2 causes a 3–54% decrease in carbonate production.

It had been conjectured by some authors that the decrease due to declining concentrations of carbonate ions may get more than offset by increases in calcification due to the increase in ocean temperature (Lough and Barnes, 2000; McNeil et al., 2004). These conjectures were based on the assumption that calcification increases in direct proportion to temperature, but all experimental studies under the laboratory and the field conditions done so far have shown that coral calcification reaches a maximum at or just below present-day temperatures (Kleypas et al., 2005). Other suggestions that coral reefs may migrate or expand significantly to higher latitudes as seas warm has been countered by the observation that carbonate ion concentrations decrease toward the poles and will reach even lower values at high latitudes than is the case now as atmospheric CO_2 increases (Kleypas et al., 2001). This, and the fact that light for photosynthesis also decreases at higher latitudes, suggests that the region in which coral reefs can survive will remain within a few hundred kilometers of where it is today.

The combined impact of elevated sea temperature and atmospheric CO_2 is likely to produce major changes in coral reefs over the next few decades. Under most IPCC emission scenarios (IPCC, 2000, 2007), corals may become rare on tropical and subtropical reefs by the middle of this century if CO_2 doubles or triples above present levels. Over longer time scales, reef frameworks that are critical for the protection of coastlines across tropical and subtropical regions may start to disappear as the rate of erosion starts to exceed calcification rates (Burke and Maidens, 2004). Biosphere II mesocosm experiments have confirmed that net reef dissolution may outpace net reef calcification when carbonate ion concentration decreases to about $150\text{--}110 \mu\text{mole kg}^{-1}$, a range that corresponds to atmospheric CO_2 concentrations of $560\text{--}840 \text{ ppmv}$. More recent estimates, based on calcification rates of over 9000 reef locations, indicate that by the time atmospheric partial pressure of CO_2 reaches 560 ppm all coral reefs will cease to grow and start

to dissolve (Silverman et al., 2009). Andersson et al. (2009), based on continuous flow mesocosm studies, suggest that some net calcifying communities could become subject to net dissolution in response to anthropogenic ocean acidification within this century. Edmunds (2007) has documented a decline in the growth rates of juvenile scleractinian corals in the U.S. Virgin Islands and has raised the possibility that the effects of global climate change (increased seawater temperatures and decreasing aragonite saturation state) have already reduced the growth rate of juvenile corals.

As it is, coral reefs have been jeopardized since several decades by overfishing and destructive fisheries, coastal construction, increased runoff and sedimentation, pollution, and introduction of nonindigenous invasive species. Then major harm was caused by global warming. Now ocean acidification appears to be the proverbial last straw, as it is being seen to exert a synergistic effect, alongside global warming, on the degradation of coral reefs (Anthony et al., 2008).

All in all, the net response of coral reef calcification to changing seawater chemistry will be the sum of many interrelated processes such as (a) the response of calcifying organisms, (b) changes in inorganic processes of carbonate precipitation and dissolution, and (c) the response of bioeroders to changes in community structure and perhaps in cementation patterns.

Coral reefs had played a key role in reducing the energy of wave impacts during the December 2004 tsunami. Those of the coastlines that did not have well-developed coral reefs had suffered greater damage to infrastructure and greater loss of life (Brown, 2004).

As for cold-water coral systems, they are found in almost all the world's oceans and seas: in fjords, along the edge of the continental shelf, and around offshore submarine banks and seamounts (Freiwald et al., 2004). Although frequently referred to as deep-water corals, they occur over a wide depth range, from a few tens of meters to over 1000 m. Their distribution is probably mainly determined by temperature, as is reflected by some occurrences in shallow water at high latitudes and exclusively deep-water occurrences in tropical and subtropical waters. The full extent of the area covered by cold-water coral ecosystems is unknown, but recent studies indicate that it could equal, or even exceed, that of warm-water reefs (Freiwald et al., 2004; Freiwald and Roberts, 2005; Guinotte et al., 2006; Turley et al., 2007). Numerous new species were recently discovered in cold-water coral ecosystems; others found in association with them were previously thought to be extinct. Indeed cold water corals bioherms have extremely high biodiversity and provide habitat and nursery areas for many deep-sea organisms, including several commercially important fish species (Fossa et al., 2002; Husebo et al., 2002; Rogers, 1999). Stone (2006) reported that 85% of the economically important fish species observed on submersible transects in waters off the Aleutian Islands were associated with corals and other emergent epifauna.

The cold-water coral *Lophelia pertusa* is one of the few species able to build reef-like structures and a three-dimensional coral framework in the deep oceans. Maier et al. (2009) collected colonies of *L. pertusa* and assessed calcification rates and how those changed due to reduced pH. The highest calcification rates were found in the youngest polyps. Lowering pH by 2.15 and 0.3 units relative to the ambient level resulted in calcification being reduced by 30 and 56%, respectively. Lower pH reduced calcification more in fast growing, young, polyps (59% reduction) than in older polyps (40% reduction). Interestingly *L. pertusa* exhibited positive net calcification (as measured by ^{45}Ca incorporation) even at an aragonite saturation state below 1.

Even though, so far, there are few other studies on the sensitivity of cold-water corals to CO_2 -related changes in seawater chemistry, it is reasonable to expect that calcification of cold-water corals will also be reduced as carbonate super-saturation declines. Because the carbonate saturation state generally decreases with latitude and water depth, the conditions in waters typically inhabited by cold-water corals are even less favorable to start with, for calcification than warm-water corals. This may cause cold-water corals to be affected earlier and more strongly by CO_2 related ocean acidification than their warm-water counterparts. Model calculations, based on a situation where CO_2 emissions continue on present trends, indicate that the aragonite saturation horizon (the depth below which aragonite dissolves) will rise closer to the oceans' surface by several hundred meters for most of the ocean, and may reach the surface in the Southern Ocean by the year 2100 (Caldeira and Wickett, 2005). Thus, not only is the ocean-wide decrease in the aragonite saturation level likely to decrease cold-water coral calcification but also large areas of the oceans may also become completely uninhabitable for cold-water corals as the impacts of increased CO_2 are greater at higher latitudes.

Indeed even with IPCC business-as-usual CO_2 emission scenarios (Orr et al., 2005), the cold high-latitude surface waters typical of the subarctic North Pacific and North Atlantic, and the Subantarctic and polar regions of the Southern Ocean, would face aragonite and calcite undersaturation in the near future when pCO_2 reaches 600 and 900 μatm , respectively. Some deep sea corals may experience undersaturated waters as early as the year 2020 (Guinotte et al., 2006), and these organisms may thus be impacted by undersaturated waters before their potential ecological and economical importance as fish habitat can be determined. In the warm tropical and subtropical waters undersaturation will occur when pCO_2 values reach about 1700 and 2800 μatm , respectively. If CO_2 emissions continue as projected, aragonite-undersaturated regions will develop in the Subarctic, Subantarctic, and polar surface waters by the end of the 21st century. This would occur first in the wintertime when surface water temperatures are coldest and pCO_2

values are highest due to wind-driven mixing of subsurface waters into the mixed layer. Undersaturated regions would then expand toward the equator.

The harm to coral reefs will adversely impact the biodiversity and function of associated ecosystems (sea grass, mangrove). The implications of these changes for people and industries is likely to be significant.

6.3 Planktonic Calcifying Organisms

The most abundant planktonic calcifying organisms are coccolithophores and foraminifera, which make calcite, and euthecosomatous pteropods, which form shells of aragonite (Bernard and Froneman, 2009; Moy et al., 2009). While many other calcifying invertebrate and protist taxa also have planktonic stages, these three groups largely account for the majority of the total CaCO_3 produced by planktonic organisms. Their attributes of mineral form, trophic level, generation time, and other aspects of their biology are presented in Table 2.

Several laboratory and field studies show that coccolithophore species may have reduced calcification rates at elevated pCO_2 , even when the calcite saturation state is >1 (Delille et al., 2005; Engel et al., 2005; Riebesell et al., 2000; Sciandra et al., 2003; Zondervan et al., 2002; Zondervan et al., 2001). In a mesocosm bloom experiment with *Emiliania huxleyi* cultured at glacial, present-day, and year 2100 CO_2 values, organic carbon production did not change, but calcification decreased under the projected year 2100 levels (Delille et al., 2005). Contrary to findings in laboratory experiments (e.g., Riebesell et al., 2000), no malformations of the coccospheres were observed, but coccospheres and coccoliths were smaller and coccoliths weighed less when grown under high pCO_2 levels (Engel et al., 2005).

In laboratory experiments with three species of planktonic foraminifera, shell mass in two species decreased as the carbonate ion concentration of seawater decreased (Bijma et al., 2002; Bijma et al., 1999; Spero et al., 1997). Data for a single species of shelled pteropod suggest that net shell dissolution occurs in live pteropods when the aragonite saturation is forced to <1 (Feely et al., 2004; Orr et al., 2005).

Foraminifera are important in global ocean calcification in both the plankton and in bottom-dwelling environments. Their calcification starts with the encapsulation of seawater (Erez, 2003). During the calcification process the alkalinity of the captured water is lowered (the pH decreases). To compensate for this the organism raises the pH, which immediately increases the carbonate ion (CO_3^{2-}) concentration. If the pH of the ambient water is to decrease (due to ocean acidification) this process will require more energy. This is perhaps the reason why calcification is adversely effected by decreasing pH. Allocating more energy to calcification to counteract the effect of decreasing pH could also mean that less energy would be available for other

vital metabolic processes, which may reduce the growth and fitness of the organism.

In laboratory experiments on the symbiont-bearing foraminiferans, a strong reduction in the calcification rate occurred as pH decreased from 9 to 7. The trend reversed only above pH 9. A positive correlation between foraminiferal shell weight and the carbonate ion concentration (and the carbonate saturation state) is also observed in the palaeoceanographic record as a response to glacial–interglacial changes in atmospheric CO₂ of the past 50000 years (Barker and Elderfield, 2002). Plotting calcification rate versus the carbonate ion concentration reveals a similar slope, with a two- to threefold increase in calcification rate, with CO₃²⁻ increasing from 100 to 400 μM.

De Moel et al. (2009) used shells of the surface water dwelling planktonic foraminifer *Globigerinoides ruber* in order to test the hypothesis that anthropogenically induced acidification has reduced shell calcification of this species. They found that light, thin-walled shells from the surface sediment are younger (based on ¹⁴C and ¹³C measurements) than the heavier, thicker walled shells. Shells in the upper, bioturbated sediment layer were significantly lighter compared to shells found below this layer. These observations are consistent with a scenario where anthropogenically induced ocean acidification reduced the rate at which foraminifera calcify, resulting in lighter shells. Plankton tow and sediment trap data collected by the same authors showed that lighter shells were produced during upwelling and heavier ones during non-upwelling periods, indicating that probably both the processes of acidification and seasonal upwelling are responsible for the presence of light shells in the top of the sediment.

It is noteworthy that while the relationship between calcification and carbonate ion concentration appears to be linear in corals, the response of other major groups of planktonic calcifiers may not be linear. Some experimental data suggests that calcification in coccolithophores and foraminifera may respond asymptotically to carbonate ion concentration. This implies that reduction of the carbonate saturation state below a threshold value will cause larger decreases in calcification rates of coccolithophores and foraminifera than it will cause for corals.

Data for a single species of shelled pteropods suggest that net shell dissolution occurs in live pteropods when the aragonite saturation is forced to <1.0 (Fabry, 2008; Orr et al., 2005). When live pteropods (*Clio pyramidata*) were collected in the subarctic Pacific and exposed to a level of aragonite undersaturation similar to that projected for Southern Ocean surface waters by the year 2100 under the IS92a emissions scenario, shell dissolution occurred within 48 hr even though the animals were actively swimming.

If high-latitude surface waters do become undersaturated with respect to aragonite, pteropods could eventually be eliminated from such regions that may strongly impact food web dynamics and other ecosystem processes

(Fabry, 2008). It may also adversely effect oceanic uptake of CO₂ (Guinotte and Fabry, 2008).

6.4 Calcified Larger Animals

The larvae of sea urchins and also of mollusks have been shown to form skeletal parts consisting of magnesium-bearing calcite that form through an amorphous precursor phase, which is 30 times more soluble than calcite without magnesium (Hunt et al., 2008; Politi et al., 2004). The same type of skeletal material is used by most adult echinoderms. Lower pH in the oceans may inhibit the formation of these highly soluble amorphous calcite precursors, which echinoderms need in the construction of their shells. Hence echinoderms are among several groups that may be especially sensitive to ocean acidification.

Several studies have demonstrated physiological stress in organisms exposed to high pCO₂ levels (Brewer et al., 2004), but recent studies have also investigated the effects of long-term exposure of mollusks and sea urchins to much lower elevations of CO₂. Green et al. (2004) found that newly settled larvae of the mollusk *Mercenaria mercenaria* experienced higher shell dissolution and mortality rates when the pore water interface was undersaturated with respect to aragonite. Specimens of *Mytilus galloprovincialis* that were maintained for three months at pH 7.3 (consistent with a pCO₂ of about 1900 μ atm) experienced a significant reduction in growth, as well as shell dissolution, in response to reduced haemolymph bicarbonate levels (Michaélidis et al., 2005). In another study, specimens of two species of sea urchin (*Hemicentrotus pulcherrimus* and *Echinometra mathaei*) and one gastropod mollusk (*Strombus luhuanus*) that were exposed for 6 months to CO₂ levels elevated by 200 ppmv over normal levels had smaller size and body weight, and in *E. mathaei*, a thinning of the CaCO₃ layers was observed (Kleypass et al., 2006; Shirayama and Thornton, 2005).

According to Gazeau et al. (2007), the calcification rates of the mussel (*Mytilus edulis*) and Pacific oyster (*Crassostrea gigas*) can be expected to decline linearly with increasing pCO₂, 25% and 10%, respectively, by the end of the century. Both species are important coastal ecosystem engineers and represent a significant portion of global aquaculture production. Bivalves that settle in coastal estuarine areas may be particularly vulnerable to anthropogenic ocean acidification. These organisms naturally experience extremely high mortality rates (> 98%) in their transition from larvae to benthic juveniles (Green et al., 2004), and any increase in juvenile mortality due to ocean acidification could have serious effects on estuarine bivalve populations. It has been demonstrated that increased pCO₂ of seawater projected to occur by the year 2300 (pH 7.4) will severely impact the early development of the oyster *Crassostrea gigas* (Kurihara and Shirayama, 2004; Kurihara et al., 2007; Kurihara et al., 2004a, 2004b, 2004c). These studies have highlighted

the importance of acidification effects on larval development stages of marine calcifiers. Fluctuations in larval stages due to high mortality rates may exert a strong influence on the population size of adults, because early life stages appear to be more sensitive to environmental disturbance than adults and most benthic calcifiers possess planktonic larval stages.

Bibby et al. (2007) documented interesting behavioral, metabolic, and morphological responses of the intertidal gastropod *Littorina littorea* to acidified seawater (pH 6.6). This marine snail produced thicker shells when exposed to predation (crab) cues in control experiments, but this defensive response was disrupted when pH was decreased. The snails also displayed reduced metabolic rates and an increase in avoidance behavior, both of which could have significant ecosystem implications via organism interactions, energy requirements, and predator–prey relationships.

Another *Littorina* species, *L. obtusata*, also exhibited reduced viability and increased development times under reduced pH conditions, and the embryos had significantly altered behaviors and physiologies (Ellis et al., 2009). In acidified seawater, embryos spent more time stationary, had slower rotation rates, and spent less time crawling, but increased their movement periodicity compared with those maintained under control conditions. Larval and adult heart rates were significantly lower in acidified seawater, and hatchling snails had an altered shell morphology (lateral length and spiral shell length) compared to control snails. These observations imply that ocean acidification may have multiple, subtle effects during the early development of marine animals that may have implications for their survival beyond those predicted using later life stages.

Many other calcifying taxa are important ecologically, economically, and as components of the marine CaCO_3 cycle (e.g., calcareous green algae, echinoderms, benthic mollusks and foraminifera, bryozoans, ahermatypic corals), but few have been tested for their physiological and calcification responses to elevated CO_2 .

Some species of echinoderms are keystone predators (sea stars) or very important grazers (urchins). This is also true of coastal mollusks and arthropods, which in addition are also of great economic importance. Crustacea may be a particularly vulnerable group because of their dependence on the availability of calcium and bicarbonate ions for the mineralization of their exoskeleton after molting. In freshwater species the animals' ability to control blood pH is affected by changes in water composition in intensive culture, particularly in recirculation systems (Brown et al., 1991). Similar effects may occur in marine species.

For example, lowering pH resulted in a decrease in survival of four species of sea urchins—one tropical (*Tripneustes gratilla*), two temperate (*Pseudechinus buttoni* and *Evechinus chloroticus*), and one polar (*Sterechinus neumayeri*) species (Clark et al., 2009). The sizes of larvae were reduced at lowered pH, but the external morphology was unaffected. Calcification of

the larval skeleton was significantly reduced (13.8–36.9% lower) under low-er pH, with the exception of the Antarctic species, which showed no significant difference. SEM examination revealed a degradation of the larval skeletons of *Pseudechinus* and *Evechinus* when grown in reduced pH, but *Sterechinus* and *Tripneustes* showed no such effect. The study points to the need to look beyond mortality as a single endpoint when considering the effects of ocean acidification that may occur through the 21st century. Instead, attempts should be made to look for a suite of more subtle changes, which may indirectly affect the functioning of larval stages.

In a field study, Tunnicliffe et al. (2009) investigated the clusters of the vent mussel *Bathymodiolus brevior* at pH values between 5.36 and 7.29, which naturally occur on the northwest Eifuku volcano, Mariana arc, where liquid carbon dioxide and hydrogen sulfide emerge in a hydrothermal setting. They found that both shell thickness and daily growth increments in shells from northwest Eifuku were only about half those recorded from mussels living in water with pH 7.8. Low pH may therefore also be implicated in metabolic impairment. They identified four-decade-old mussels, but suggest that the mussels could have survived for so long only because their protective shell covering would have remained intact; crabs that could expose the underlying calcium carbonate to dissolution were absent from this setting. The mussel's ability to precipitate shells in such low-pH conditions appeared remarkable, but the vulnerability of mollusks to predators is likely to increase in an increasingly acidified ocean.

McDonald et al. (2009) examined larval condition, cyprid size, cyprid attachment and metamorphosis, juvenile to adult growth, shell calcium carbonate content, and shell resistance to dislodgement and penetration in the barnacle *Amphibalanus amphitrite* reared from nauplii in either ambient pH 8.2 seawater or under CO₂-driven acidification of seawater down to a pH of 7.4. There were no effects of reduced pH except that barnacles exposed to pH 7.4 displayed a trend of larger basal shell diameters during growth, suggestive of compensatory calcification. Furthermore, greater force was required to cause shell breakage of adults raised at pH 7.4, indicating that the lower, active growth regions of the wall shells had become more heavily calcified. Ash contents (predominately calcium carbonate) of basal shell plates confirmed that increased calcification had occurred in shells of individuals reared at pH 7.4. Significantly, despite enhanced calcification, penetrometry revealed that the central shell wall plates required significantly less force to penetrate than those of individuals raised at pH 8.2. Thus, dissolution seem to have rapidly weakened wall shells as they grow. The ramifications of these observations at the population level are important, as barnacles with weakened wall shells are more vulnerable to predators.

7. IMPACT ON OTHER OCEANIC HABITAT AND ORGANISMS

7.1 Pelagic Habitat

As much as 99% of the organic matter used by marine food webs is produced by photosynthetic marine organisms converting dissolved CO₂ to organic carbon. They account for a little less than half of the total primary productivity on Earth. The vast majority occur as free-floating microscopic phytoplankton, over the whole of the surface oceans. They fix about 50 Gt (giga tons) of carbon per year into their bodies with significant additional extracellular dissolved organic carbon (Engel et al., 2004). Most of the organic matter produced by these photosynthetic organisms is immediately or ultimately consumed by other microorganisms.

Rich and diverse communities of coccolithophores, foraminifera, and pteropods inhabit the sunlit (euphotic) zone of all open and coastal ocean areas, with the exception of the Southern Ocean and the Arctic (De Moel et al., 2009; Dupont and Thorndyke, 2009). Massive blooms of coccolithophores, which can cover hundreds of thousands of square kilometers of surface oceans and can each produce up to one million tons of calcite (Holligan et al., 1993; Raven et al., 2005); are known to occur (Iglesias-Rodriguez et al., 2002). Even outside these blooms, which are predominantly formed by only one species, *Emiliania huxleyi*, coccolithophores are a common and often dominant component of the phytoplankton community (for example in subtropical circulation currents). Laboratory and field experiments have shown that calcification of coccolithophores decreases with decreasing saturation state (Riebesell et al., 2000; Zondervan et al., 2001).

As has been shown in studies described in the preceding section, calcification of foraminifera, a group of calcite-producing protists is also likely to be effected by ocean acidification (Bernhard et al., 2009). As with other calcifying organisms, changes to the distribution and abundance of these protists could have significant effects on the global carbon cycle. It may be expected that calcifying organisms in near-polar areas, where saturation state is the lowest, will be affected in the nearest future. Owing to the higher solubility of aragonite the pteropods, that produce CaCO₃ in its aragonite form, will be more strongly affected than the coccolithophores and foraminifera that produce the calcite form. If CO₂ emissions continue on present trends the aragonite saturation horizon will rise to the surface of the oceans before the end of this century, making aragonite skeletons unstable throughout the water column over the entire Southern Ocean.

If the community structure shifts from coccolithophore to a diatom-dominated phytoplankton community, or vice versa, it can have strong impacts on the entire ecosystem of the region where it occurs. In the eastern Bering Sea such a regime shift occurred in the late 1990s. One of the results of this was a strong decline in salmon catches during these years. Evidence of shifts in marine community structure due to the stressor of ocean

acidification is being increasingly found in field studies (Hall-Spencer and Rodolfo-Metalpa, 2009; Munday et al., 2009; Tunnicliffe et al., 2009).

7.2 Benthic Habitat

The benthic (bottom-dwelling) photosynthetic organisms, such as seaweed, sea grasses, and corals, are the other major primary producers in the oceans. Limited to shallower waters, they have a net primary productivity of about 1 Gt of carbon per year (Field et al., 1998). Despite their limited role in global primary productivity, these benthic primary producers are crucial components of coastal ecosystems, providing habitats and breeding grounds for other species, as well as recycling nutrients and reducing coastal erosion by reducing the power of waves.

In shallow (less than 50 m) coastal areas productivity in the overlying water column relies on the sediment system, with up to 80% of the nitrogen required by phytoplankton coming from the bacterial regeneration of organic matter within the seabed (Dale and Prego, 2002). In other regions of the oceans, sediment-dominated habitats, which occupy a large fraction of the area of the oceans, play a crucial role in several key ecosystem functions and processes. Of particular concern are the abyssal ecosystems that occur in the ocean depths below 3000 m (Gage and Tyler, 1991). Abyssal ecosystems cover about 54% of the earth's surface, which makes them truly vast. They have no in situ primary production (except at spatially rare hydrothermal vents and cold seeps), which makes them food-limited because their zoomass production depends on the input of detrital organic material produced in the euphotic zone thousands of meters above (Figure 6). Most of the organic flux arrives at the abyssal region as an attenuated rain of small particles (typically, only 0.5–2% of net primary production in the euphotic zone). It, too, decreases inversely with water depth and varies regionally with levels of primary production in the upper ocean. The small particle flux is only occasionally augmented by the fall of larger carcasses, or by the down slope transport of organic material near continental margins (Smith and Demoupolos, 2003).

Global extrapolations suggest that due to the vast size of the abyssal region it may be a major reservoir of biodiversity (Bouchet, 2006). The enormous abyss also provides important ecosystem services, exerting significant influence on ocean carbon cycling, calcium carbonate dissolution and atmospheric CO₂ concentrations over timescales of 100–1000 years.

Considering that many aspects of ecosystem structure and function in the abyss are strongly modulated by the rate and nature of food flux to the seafloor, climate change and anthropogenic ocean fertilization will substantially alter productivity patterns in the surface ocean and in turn the flux of food material to the abyss; this may profoundly affect abyssal ecosystem

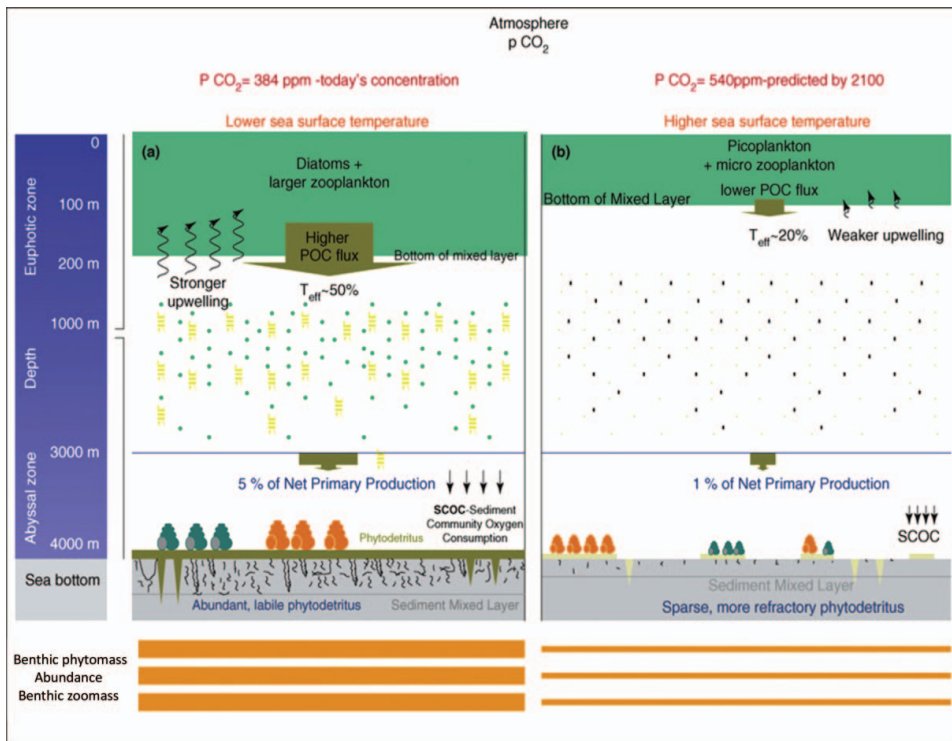


FIGURE 6. Impact of CO₂-forced 'thinning' of euphotic zone on benthic habitat; it would reduce the import of net primary production to the abyssal zone several times from the normal ca 5%, with cascading negative impacts (adopted from Smith et al., 2008) (Color figure available online).

structure and function (Figure 6), altering patterns of diversity and ecosystem services (Smith et al., 2008).

Biogeochemical changes in the upper ocean resulting from global warming include increased sea-surface temperatures and thermal stratification, as well as reductions in nutrient upwelling. The magnitude of such effects are likely to be substantial because ocean warming to date appears to have caused a 6% decline in global ocean primary production (Gregg et al., 2003). These impacts are exacerbated by ocean acidification. The cumulative effects of all these stressors over regional scales are likely to be greater reductions in primary production as well as a shift from diatom-based phytoplankton assemblages with high export efficiencies to picoplankton assemblages characterized by low export of primary production to the abyss (Smith et al., 2008).

Moreover, benthos, which inhabit permanent burrows, have a greater tolerance to changes in pH than those that do not build burrows. This difference in pH tolerance within benthic species can lead to the predominance of more tolerant species and thinning of the more sensitive species, thereby substantial changes in the structure and function of sediment communities. Recent work has already identified significant variability in pH sensitivity for several different benthic groups (McClintock et al., 2009; Shirayama et al., 2004). Even among organisms that depend on CaCO_3 structures, variability in tolerance has been observed with echinoderms showing less tolerance to pH change than mollusks (Shirayama et al., 2004). Decreases in calcification rates across a suite of benthic species and calcifying systems range from 3 to 60% for a doubling in pCO_2 (34% reduction in saturation state). The average response of corals is a 30% decline in calcification in response to a doubling in pCO_2 (Table 3). Such differences in the response of organisms from different taxa and functional groups to reduced pH could have a considerable impact on the functioning of marine sediments. Consequently, while changes in seawater pH may have a direct effect on sediment and seawater chemistry through changes in nutrient speciation, this effect may snowball due to more and more species being impacted, directly or indirectly.

An examination of the postmortem dissolution rates of aragonitic and calcitic shells from four species of Antarctic benthic marine invertebrates, carried out by McClintock et al. (2009), revealed that within a period of only 14–35 days, shells of all four species held in pH 7.4 seawater had suffered significant dissolution. Despite calcite being 35% less soluble in seawater than aragonite, there was, surprisingly, no consistent pattern of calcitic shells having slower dissolution rates than aragonitic shells. Outer surfaces of shells held in pH 7.4 seawater exhibited deterioration by day 35, and by day 56 there was exposure of aragonitic or calcitic prisms within the shell architecture of three of the macroinvertebrate species. Dissolution of coralline algae was confirmed by differences in weight loss in limpet shells with and without coralline algae. By day 56, thalli of the coralline alga held in pH 7.4 displayed a loss of definition of the conceptacle pores and cracking was evident at the zone of interface with limpet shells. These findings again underscore the need for experimental studies to evaluate whether there are adequate compensatory mechanisms in these and other calcified Antarctic benthic macroorganisms to cope with anticipated ocean acidification. In their absence, these organisms, and the communities they comprise, are likely to be among the first to experience the cascading impacts of ocean acidification.

Interestingly, Arnold et al. (2009) reported that a critical appraisal of calcification in six benthic species by them showed that calcification can increase, and not always decrease, in acidified seawater. Measuring the changes in calcium in isolated calcium carbonate structure as well as structures from live animals exposed to acidified seawater by the authors enabled a comparison between a species' ability to calcify and the dissolution affects

across decreasing levels of pH. The authors found that calcium carbonate production was dependant on the ability to increase calcification thus counteracting an increase in dissolution, and comparison with paleoecological studies of past high carbon dioxide (CO₂) events presented a similar picture. This conclusion implies that the physiological trade-offs, including reduced metabolism, health, and behavioral responses, displayed by all the species as a response to hypercapnia, investigated by Arnold et al. (2009), indicate as great a threat to survival as an inability to calcify.

The nature and roles of the oceanic plankton and benthos, with reference to calcification, are shown in Table 6.

7.3 Larger Animals

Further up the marine food webs are the multicellular animals. Although these are dependent on the availability of the microorganisms for food, and are therefore affected indirectly by changes in ocean carbon chemistry, the physiology of these relatively more complex organisms may also be affected directly by changes in ocean chemistry. They would also face indirect consequences of the ocean acidification in the form of changing food webs and predator–prey interactions.

EFFECT ON PHYSIOLOGY

With the exception of animals that have accessory organs capable of breathing air, most marine fish and the larger invertebrates, including some zooplankton, take up oxygen and lose respired CO₂ only from the water through their gills. Increased CO₂ and decreased pH could have a major effect on this respiratory gas exchange system. This is because oxygen is much harder to obtain from surface seawater than it is from air; the dissolved oxygen (DO) concentration in seawater, at normal temperature (25°C) is just about 12 mg/L. The processes involved in supplying oxygen to the gills means that more CO₂ is removed from these aquatic animals than is removed from air-breathing animals of a similar size. This, in turn, means that the level and range of CO₂ concentration in the bodies of water-breathing animals are much lower than air-breathing animals. As a result, large water breathing marine animals are more sensitive to changes in the CO₂ concentration in the surrounding seawater than are large air-breathing animals. Moreover, increased CO₂ is likely to acidify the body tissues and fluids and affect the ability of blood to carry oxygen.

The acidification of body fluids of marine animals (hypercapnia) occurs quickly as a result of increasing external CO₂—in a matter of hours. In addition to reducing the pH, increased CO₂ concentration also changes the levels of bicarbonate and other ions. Small changes can be buffered within the cell, but larger changes require the active secretion of ions out of the

TABLE 6. Nature and roles of the oceanic plankton and benthos with special reference to calcification (adopted from Kleypass et al., 2006)

Feature	Benthos	Plankton
Ecology Habit	Mostly stationary or sedentary as adults; CaCO ₃ accumulation provides structural ecosystem framework	Nonstationary; CaCO ₃ accumulation physically separate from ecosystem
Domain	Continental shelves <100 m deep; mostly at low latitudes; abyssal benthos occur >3000 m depths	Upper ocean; present data suggest mostly at high latitudes
Nutrient limitation	Usually low; much higher for abyssal benthos	Variable
Light limitation	Many species are photosynthetic or have photosynthetic symbionts; abyssal benthos are nonphotosynthetic	Many species are photosynthetic or have photosynthetic symbionts
Temperature limitation	Directly affected by changing temperature	Indirectly affected by changes in thermal stratification, upwelling
Biodiversity/functional diversity	High	High at low latitudes; generally lower at high latitudes
Influence of sedimentary processes	Much higher	Lower
Dominant calcifiers	Coelenterates/algae at low latitudes; bryozoans, mollusks, forams, algae, at temperate latitudes	Algae, protists, mollusks
Food web	Some primary producers, some only consumers	Primary producers, consumers
Competition stress	Potential to be outcompeted by noncalcifying species	Potential to be outcompeted by noncalcifying species
Response to pCO ₂ variability	High	Lower
Capacity to adapt to elevated pCO ₂	No evidence of adaptation in corals, coralline algae	Not certain—short generation times may enhance ability to adapt
Calcification: Production cycle/generation times	Relatively constant production: Regeneration times usually years to decades	Variable production cycle from bloom-forming to relatively constant; regeneration times usually days to months
Mineralogy	Low latitudes: mainly aragonite (corals) and high-Mg calcite (calc. algae) High latitudes: mainly calcite (bryozoans, forams) and mixed aragonite/calcite (mollusks)	Mainly calcite (coccolith; forams; some aragonite (pteropods; heteropods); some high-Mg calcite
Area	~1 × 10 ¹² m ² (excluding abyssal region which is about 54% of all land area)	~300 × 10 ¹² m ²
Calcification rate	10–180 g Cm ⁻² Y ⁻¹	1–2 g C m ⁻² y ⁻¹
Net CaCO ₃ production	0.02–0.1 Pg Cy ⁻¹	0.29–1.1 Pg C y ⁻¹
Net CaCO ₃ accumulation	0.01–0.1 Pg Cy ⁻¹	0.1 Pg C y ⁻¹

body through specialized cells. There is strong experimental evidence that acidosis of tissues will decrease cellular energy use and lower respiratory activity (Pörtner et al., 2000; Pörtner et al., 2004). Evidence is also increasing of lower rates of protein synthesis under these conditions, with impacts on almost all aspects of the functioning of larger animals including growth and reproduction (Langenbuch and Pörtner, 2002, 2003). Experiments have shown that rising external atmospheric CO₂ increases mortality, and in some cases quite significantly (Kikkawa et al., 2004).

Deep-sea fish and cephalopods such as squid are particularly sensitive to increases in external CO₂ (Ishimatsu et al., 2004). Squid are vulnerable because of their highly muscular and energy-demanding way of movement (jet propulsion), which is fundamentally different from the lower energy demands of undulatory swimming seen in fish (Pörtner and Zielinski, 1998). This high-energy use requires a good supply of oxygen from the blood. However, this can be severely compromised by increasing CO₂ concentration, as it lowers the pH of the blood thereby reducing its ability to carry oxygen.

In a report which has stirred a good deal of controversy, Wilson et al. (2009) suggested that marine fish produce precipitated carbonates within their intestines and excrete these at high rates. When combined with estimates of global fish biomass, this suggests that marine fish contribute 3–15% of the total oceanic carbonate production. According to the authors, fish carbonates have a higher magnesium content and solubility than traditional sources, yielding faster dissolution with depth, and that this may explain up to a quarter of the increase in titratable alkalinity within 1,000 m of the ocean surface, a phenomenon that has puzzled oceanographers for decades. Wilson et al. (2009) also predicted that fish carbonate production may rise in response to future environmental changes in carbon dioxide, and thus become an increasingly important component of the inorganic carbon cycle.

EFFECT ON REPRODUCTIVE BEHAVIOR

Controlled experiments have shown that in freshwater fish, increased levels of CO₂ and decrease in pH affects the physiology and activation of sperm. In steelhead trout (*Oncorhynchus mykiss*), for example, decreasing pH from 8.5 to 7.5 units by increasing the partial pressure of CO₂ resulted in a 40% reduction in respiration rate (Ingermann et al., 2003). Significant loss (40%) of sperm motility of Pacific oysters (*Crassostrea gigas*) has been shown in laboratory experiments during changes in pH from 8 to 6 units (Dong et al., 2002). Even though this extent of change in pH is beyond any expected projections for oceans, long-term exposures to even lesser changes in pH can have similar effects in real-life situations. Experiments have also demonstrated significant decrease in egg production by copepods, but no effect on

survival of adults, over the 8-day test period (Kurihara et al., 2004a, 2004b). In another experiment, lower pH decreased hatching of the egg sacs of a gastropod mollusk (*Babylonia areolata*) farmed in the Far East (Luo et al., 2004). Other studies using high concentrations of CO₂ have also shown effects on the embryos and larvae of silver sea bream (*Pagrus major*; Ishimatsu et al., 2004) and on the reproduction in sea urchins (Kurihara et al., 2004a). These experiments suggest that the early stages of the life cycle may show the greatest sensitivities to increased CO₂ concentrations, with potentially widespread implications for population size, community structure and biodiversity.

EFFECTIVE ON OLFACTORY STIMULI

The survival of most coastal marine species depends on larvae finding suitable adult habitat at the end of an offshore dispersive stage that can last weeks or months. Munday et al. (2009) tested the effects that ocean acidification from elevated levels of atmospheric carbon dioxide (CO₂) could have on the ability of larvae to detect olfactory cues from adult habitats. Larval clownfish reared in control seawater (pH 8.15) discriminated between a range of cues that could help it locate reef habitat and suitable settlement sites. This discriminatory ability was disrupted when larvae were reared in conditions simulating CO₂-induced ocean acidification. The larvae became strongly attracted to olfactory stimuli they normally avoided when reared at levels of ocean pH that could occur in the year 2100 (pH 7.8) and they no longer responded to any olfactory cues when reared at pH levels (pH 7.6) that may be attained later next century on a business-as-usual carbon dioxide emissions trajectory. It may be expected that if acidification continues unabated, the impairment of sensory ability may reduce population sustainability of many marine species, with potential consequences for marine diversity.

7.4 Indirect Impacts on Species Balance

Exposure of macrofaunal and nematode assemblages to acidified seawater significantly alters community structure and reduces diversity (Widdicombe et al., 2009). However, the impact on nematodes is less severe than that on macrofauna. In a field study by the authors, the communities in both sediment types were found to be significantly affected by changes in seawater pH, but impacts on sandy sediment fauna were greater than those on muddy sediment fauna. Sandy sediments also showed the greatest effects with respect to nutrient fluxes. In sand, the efflux of nitrite, nitrate, and silicate decreased in response to increased acidification while the efflux of ammonium increased. In mud, acidification increased the efflux of ammonium but had no effect on the other nutrients. Apparently, lowered seawater

pH could also affect nutrient cycling directly by altering bacterial communities and indirectly through impacts on the abundance and activity of key bioturbators.

A carbonate budget based on several studies of the bryozoan *Adeonellopsis* in Doubtful Sound, New Zealand (Smith, 2009) showed that increasing dissolution pressure in cool temperate environments dramatically reduces sediment accumulation rates. This indicates that bryozoan shelf carbonate sediments, which blanket the southern shelves of New Zealand and Australia, may serve as biological saturoimeters, monitoring the effects of acidification over shelf depths. Whether acting as forewarners, models, or sentinels, bryozoans have potential in providing insight into ocean acidification.

Arnold et al. (2009) investigated the effect of culture in CO₂-acidified sea water on early larval stages of lobster *Homarus gammarus*. It did not significantly affect carapace length or development of *H. gammarus*, but there was a reduction in carapace mass during the final stage of larval development. Thus despite there being no observed effect on survival, carapace length, or zoeal progression, OA-related (indirect) disruption of calcification and carapace mass may still adversely affect the competitive fitness and recruitment success of larval lobsters with serious consequences for population dynamics and marine ecosystem function.

Another perspective on the complexity associated with the assessment of impact of ocean acidification is provided by Miller et al. (2009) on the basis of studies on veliger larvae of two oyster species, *Crassostrea virginica* and *Crassostrea ariakensis*. The larvae were grown in estuarine water under four pCO₂ regimes—280, 380, 560, and 800—to simulate atmospheric conditions in the preindustrial era, present, and projected future concentrations in 50 and 100 years, respectively. *C. virginica* experienced a 16% decrease in shell area and a 42% reduction in calcium content when preindustrial and end of 21st century pCO₂ treatments were compared. *C. ariakensis* showed no change to either growth or calcification. Both species demonstrated net calcification and growth, even when aragonite was undersaturated, a result that runs counter to previous expectations for invertebrate larvae that produce aragonite shells. Based on this, Miller et al. (2009) suggested that temperate estuarine and coastal ecosystems are vulnerable to the expected changes in water chemistry due to elevated atmospheric CO₂ and that biological responses to acidification, especially calcifying biota, will be species-specific and therefore much more variable and complex than reported previously.

The variability in the response of different species to ocean acidification is also reflected in another recent study, of Melzner et al. (2009). The authors subjected two groups of Atlantic Cod to water containing elevated CO₂ for 4 and 12 months, respectively. Measurements of standard and active metabolic rates, critical swimming speeds, and aerobic scope of long-term incubated cod showed no deviations from control values, indicating that locomotory performance was not compromised by the different levels of

chronic hypercapnia. There was evidence of adjustment in enzymatic activity to cope with the CO₂-induced acid-base load while under milder hypercapnic conditions.

Ocean acidification may enhance the dominance of some organisms that either adopt better to the acidification than most other organisms or find conditions caused by OA better suited to them. For example, jellyfish (*scyphomedusae*, *hydromedusae*, and *cubomedusae*) blooms have increased over the last several decades (Purcell et al., 2007). Attrill et al. (2007) reported a significant correlation of jellyfish frequency in the North Sea from 1971 to 1995 with decreased pH (from 8.3 to 8.1) of surface waters. They suggest that projected climate change and declining ocean pH may increase the frequency of jellyfish in the North Sea over the next century. Jellyfish are both predators and potential competitors of fish, hence abnormally large and frequent jellyfish blooms may substantially affect pelagic and coastal ecosystems (Purcell, 2005; Purcell and Arai, 2001). Continued changes in the seawater inorganic carbon system may further enhance the problematic increase in jellyfish that have already occurred due to climate change, overfishing, eutrophication, and other factors (Purcell et al., 2007).

Gooding et al. (2009) manipulated water temperature and pCO₂ to determine the effects on the sea star *Pisaster ochraceus*, a keystone predator. They found that sea star growth and feeding rates increased with water temperature. A doubling of pCO₂ concentration also increased growth rates both with and without a concurrent temperature increase. Higher pCO₂ also had a positive but nonsignificant effect on sea star feeding rates, suggesting that CO₂ concentration may be acting directly at the physiological level to increase growth rates. As in past studies of other marine invertebrates, increased CO₂ reduced the relative calcified mass in sea stars, although this effect was observed only at the lower experimental temperature. The positive relationship between growth and pCO₂ found by these authors contrasts with previous studies, most of which have shown negative effects of pCO₂ on marine species, particularly those that are more heavily calcified than *P. ochraceus*. This report gives one more indication that a few organisms may respond favorably to changing climatic variables unlike most other organisms, thereby precipitating major decline in species diversity.

Two oyster species, the Eastern oyster (*Crassostrea virginica*), and the Suminoe oyster (*Crassostrea ariakensis*) when grown in estuarine water under four pCO₂ regimes—280, 380, 560, and 800, respectively (Miller et al., 2009)—also displayed widely different response. *C. virginica* had a 16% decrease in shell area and a 42% reduction in calcium content when at elevated pCO₂ treatments but *C. ariakensis* showed no change to either growth or calcification. Both species demonstrated net calcification and growth, even when aragonite was undersaturated, a result that runs counter to previous expectations for invertebrate larvae that produce aragonite shells. The results

reinforce the emerging understanding that biological responses to acidification, especially calcifying biota, will be species-specific and therefore much more variable and complex than reported previously.

8. SYNERGISTIC IMPACTS OF MULTIPLE STRESSORS

Increasing attention is being paid to the assessment of simultaneous impacts of one or more stressors alongside ocean acidification. The findings reveal that multiple stressors often act synergistically, exacerbating the harm caused by each individual stressor.

For example, Parker et al. (2009) reported synergy between the effects of ocean acidification and temperature on the fertilization and embryonic development of the oyster, *Saccostrea glomerata*. As pCO₂ increased, fertilization significantly decreased. The temperature of 26°C was optimum for fertilization, and as temperature increased and decreased from this optimum fertilization decreased. There was also an effect of pCO₂ and temperature on embryonic development. Generally, as pCO₂ increased, the percentage and size of *D-veligers* decreased and the percentage of *D-veligers* that were abnormal increased. It was clear that predicted changes in ocean acidification and temperature over the next century may have severe implications for the distribution and abundance of *S. glomerata* as well as possible implications for the reproduction and development of other marine invertebrates.

Russell et al. (2009) tested whether ocean acidification and local stressors (elevated nutrients) can combine to accelerate the expansion of filamentous turfs at the expense of calcifying algae (kelp understory). Their results indicate that they do; highlighting the synergistic effects of future CO₂ and nutrient concentrations on the abundance of turfs.

Interactive effects of warming and acidification on fertilization and development of echinoid *Heliocidaris erythrogramma* were also seen by Byrne et al. (2009). The percentage of fertilization was high (>89%) across all treatments. There was no difference in percentage of normal development in any pH treatment. In elevated temperature conditions, +4°C reduced cleavage by 40% and +6°C by a further 20%. Normal gastrulation fell below 4% at +6°C. At 26°C, development was impaired. This indicated thermotolerance and pH resilience of *H. erythrogramma* to fertilization and embryogenesis within predicted climate change scenarios, with negative effects at upper limits of ocean warming. The findings suggest that even as ocean acidification research has focused on impaired calcification, embryos may not even reach the skeletogenic stage in a warm ocean.

When larvae of sea urchins (*Strongylocentrotus franciscanus*) raised under elevated CO₂ conditions were subjected to 1 hr acute temperature stress, their ability to mount a physiological response (as measured by expression

of the molecular chaperone hsp70) was reduced relative to those raised under ambient CO₂ conditions (O'Donnell et al., 2009). These results represent one of the first uses of gene expression assays to study the effects of OA on sea urchin development, and highlight the importance of looking at multiple environmental factors simultaneously for assessing impacts of atmospheric changes.

In a study by Egilisdottir et al. (2009), reduced salinity, not pH, exerted a strong significant effect on numbers and calcium content of hatchlings of amphipod *Echinogammarus marinus* (Leach). Females exposed to low salinity did not carry eggs through to hatching. There was no significant difference in the number of viable hatchlings but the exoskeleton of the juveniles contained significantly less calcium. The authors opine that ocean acidification may affect aspects of *E. marinus* development but exposure to realistic low salinities appear, in the short term, to be more important in impacting development than exposure to CO₂-acidified sea water.

Lenton et al. (2009) explored the interaction of two important anthropogenic changes—stratospheric ozone depletion and greenhouse gas increases—and found a link. They have shown that by accounting for stratospheric ozone depletion in a coupled climate carbon model, the ventilation of carbon-rich deep water is enhanced through stronger winds, increasing surface water CO₂ at a rate in good agreement with observed trends. As per model prediction, the Southern Ocean uptake reduced by 2.47 PgC during 1987–2004, which is consistent with atmospheric inversion studies. The enhanced ventilation may also accelerate ocean acidification, despite lesser Southern Ocean CO₂ uptake. The authors suggest that studies of future climate that neglect stratospheric ozone depletion are likely to overestimate regional and global oceanic CO₂ uptake and underestimate the impact of ocean acidification.

9. EFFECT OF OCEAN ACIDIFICATION ON THE AVAILABILITY OF NUTRIENTS AND TOXINS

Besides the components of the CO₂–bicarbonate–carbonate system, several other substances are significant for life in the oceans as nutrients or as toxins. Nutrients are essential for life, whereas toxins are harmful. Most nutrients can act as toxins when present at high concentrations (e.g., the trace elements arsenic, boron, copper, and zinc). Substances such as mercury, cadmium, and pesticides are not beneficial at any level but are toxic when present beyond their safe thresholds. Ocean acidification is expected to produce changes in ocean chemistry that may affect the availability of both nutrients and toxins to marine organisms.

The chemical form of an element in seawater (its speciation) is affected by the presence of other chemical species with which it may interact. Among

these is the hydrogen ion concentration. Metals exist in seawater either in free (ionic or elemental) or bound form (as inorganic or metalloorganic compounds). It is generally the free dissolved form of the metals that is most toxic. A decrease in pH normally increases the proportion of free dissolved forms of the metals (Abbasi, 1976, 1987).

Trace element species that are strongly hydrolyzed in seawater (e.g., aluminum, iron, chromium, bismuth, uranium) and form oxyanion $[\text{MO}_x^-(\text{OH})_n]$, hydroxyl $[\text{M}(\text{OH})_n]$, or carbonate complexes are strongly influenced by variations in both temperature and pH (Abbasi, 1988a, 1988b, 1989; Byrne, 2002; Byrne et al., 1988). These changes can directly affect their bioavailability to phytoplankton. But the details of the metal speciation as a function of pH, as well as the speciation impacts on bioavailability, are not as well known for the trace elements as they are for the major and minor elements. Even less well known is the influence of pH on the multimetal-multiligand equilibria that exist in different regions of the oceans (Bruland and Lohan, 2004).

Dissolved organic matter that undergoes hydrolysis reactions in seawater (e.g., organic acids, amino acids, nucleic acids, proteins, humic materials) is also strongly influenced by changing pH, but the nature and extent of its impact on biota is largely unknown. A greater deal of research is needed on how ocean acidification will impact trace metal and organic matter speciation and biogeochemical processes in the high- CO_2 oceans of the future.

According to available reports, phytoplankton growth rates have been found to be limited by iron availability over at least 10% of the oceans' surface (Boyd et al., 2000). Reduction in pH may make available more iron than necessary and cause imbalance (Morel et al., 2003). In general, the main impact of change in pH on speciation of trace metals is to release previously bound metals from the sediment to the water column. This could be of particular importance in shallow seas.

Pointers may be drawn from theoretical speciation diagrams that allow a qualitative prediction of the effect of pH on nutrient speciation (Zeebe and Wolf-Gladrow, 2001). These show significant changes in speciation of phosphate, silicate, iron, and ammonia within the range of decrease in pH expected during ocean acidification. Reduced pH would, for example, lower the concentrations of ammonia (NH_3) in seawater in preference to ammonium (NH_4^+). In mesotrophic coastal waters with frequently high nutrient concentrations, a change of pH from 8.1 to 7.8 halves the fraction of NH_3 in the ratio of $\text{NH}_4^+ : \text{NH}_3$ (Raven, 1986).

Ocean acidification also has the potential to alter ocean biogeochemical dynamics for organic carbon and nutrients via several indirect pathways (Doney et al., 2009). Increased carbonate dissolution in the water column could decrease the contribution of CaCO_3 to the showering of organic carbon to the deep sea (Armstrong et al., 2002; Klaas and Archer, 2002;

Passow, 2004), causing more organic carbon to remineralize in shallow waters, thereby decreasing the ocean's CO₂ uptake efficiency.

Laboratory and mesocosm experiments suggest a shift toward organic matter with higher C/N ratios for individual phytoplankton species and plankton communities grown at high CO₂. This could degrade the food quality for heterotrophic zooplankton and microbial consumers.

Nitrogen-fixing cyanobacteria in the genus *Trichodesmium*, which support a large fraction of primary productivity in low nutrient areas of the world's oceans, show increased rates of carbon and nitrogen fixation and increased C/N ratios under elevated pCO₂ (Barcelos e Ramos et al., 2007; Hutchins et al., 2007). At CO₂ levels of 750 ppmv, *Trichodesmium* CO₂ fixation rates increased by 15–128% and N₂ fixation rates increased by 35–100% relative to the rates in present-day CO₂ conditions (Hutchins et al., 2007). It is expected that adoptive responses may induce similar enhancement in nitrogen fixation rates at elevated CO₂. This would provide additional new nitrogen in low-nutrient subtropical regions, zones where future primary production is expected otherwise to decline because of increased vertical stratification and reduced vertical nutrient inputs from below (Boyd and Doney, 2002). However, the actual increase in nitrogen fixation may be limited by the availability of phosphorus and iron.

10. MITIGATION OF OCEAN ACIDIFICATION

The impact of CO₂ emissions on global warming was acknowledged much before the phenomena of ocean acidification became known. As a consequence, efforts to control global warming have had a head start over efforts to mitigate ocean acidification. All those strategies to control global warming which are based on reducing CO₂ emissions—for example, improving fuel efficiency, shift to renewable energy, carbon sequestration, methane capture (Abbasi and Abbasi, 2000, 2011b, 2011c; Gajalakshmi and Abbasi, 2004a, 2004b; Ramasamy et al., 2004)—will also contribute toward slowing down (but not reversing in the foreseeable future) ocean acidification.

Other proposed efforts to reduce global warming revolve round geo-engineering or climate engineering. But while these efforts may be able to stabilize temperatures, it is generally assumed that this will not prevent continued ocean acidification (Rasch et al., 2008; Salter et al., 2008). Due to the strong coupling between climate and the carbon cycle, climate engineering could indirectly affect ocean chemistry. Matthews et al. (2009) used a global Earth-system model to investigate how climate engineering may affect surface ocean pH and the degree of aragonite saturation. They deduced that climate engineering could significantly redistribute carbon emissions among atmosphere, land, and ocean reservoirs. This could slow pH decreases somewhat relative to the nonengineered case, but would not affect the level of

aragonite saturation due to opposing responses of pH and aragonite saturation to temperature change. Moreover, these effects are subject to enhanced carbon accumulation in the land biosphere; without this, climate engineering will have little effect on pH, but would, rather, lead to accelerated declines in aragonite saturation.

It has even been argued, for example, by Bala (2009), that the proposed geoengineering schemes which attempt to reduce the amount of solar radiation absorbed by our planet could lead to a slowdown in the global hydrological cycle. This may even aggravate rather than resolve the problem of ocean acidification.

It has been suggested that some of the CO₂ may be directly injected into deeper layers of the ocean or the upper layers may be fertilized with iron to reduce accumulation of CO₂ in the atmosphere (Boyd et al., 2000; Coale et al., 1996), but these may well prove to be remedies worse than the disease, considering their potential to cause massive upsets in the ocean chemistry and biology (Cullen and Boyd, 2008; Huesemann, 2008).

There are also suggestions that some of the chemical effects of CO₂ addition could be mitigated with the addition of alkalinity to the oceans (Kheshgi, 1995; Rau and Caldeira, 1999). But this is also fraught with complications. First, if enough alkalinity were added to restore the mineral saturation state of ocean carbonate, only half of the pH change would be mitigated. But if enough alkalinity were added to restore ocean pH, the oceans would become more saturated with carbonate minerals, leading to ecosystem-level changes of unforeseen magnitude. Moreover, as elaborated subsequently, the quantities of chemicals needed to adjust the pH of systems as gigantic as the oceans would require mining at massive scales—entailing their own environmental risks.

Whichever way it is approached, the challenges in achieving mitigation at a global scale, or even a local scale are formidable. Alkalinity could be provided by highly soluble minerals such as magnesium hydroxide, Mg(OH)₂ (Kheshgi, 1995). Unfortunately, such minerals are relatively rare and unlikely to be obtained at the required scale. Consequently, attentions have focused on carbonate minerals such as limestone. But the mining and transportation of limestone at a scale adequate for neutralizing the heightened acidity of the oceans would be prohibitively large and would also require a great deal of energy. The only plausible source at present for energy of the required extent is fossil fuel; this would offset much of the mitigation efforts by contributing its own load of greenhouse gas emissions!

To counteract the changes in acidity caused by today's ocean uptake of roughly 2 Gt C per year (IPCC, 2001) would require roughly 20 Gt CaCO₃ per year (Caldeira and Rau, 2000), which, for a limestone layer 100 m thick, would require the removal of roughly 60 km² each year. Any operation of such a magnitude would invoke a host of additional environmental problems. Furthermore, limestone does not dissolve in surface waters, so additional

processing, and energy, would be needed (Kheshgi, 1995; Rau and Caldeira, 1999).

Saltwater aquarists do use carbonate minerals to promote coral growth in fish tanks, hence it is plausible to use alkalinity addition to save specific coral reefs (Rau and Caldeira, 2002). But such options have never been tested *in situ* and their efficacy under field conditions is uncertain.

Recently, Rau (2009) proposed electrochemical splitting of calcium carbonate as a method of forming hydroxide solutions that can absorb, neutralize, and store carbon dioxide from the air or from waste streams. Rau (2009) proposed to dissolve CaCO_3 in the presence of the highly acidic anolyte of a saline water electrolysis cell, forming $\text{Ca}(\text{OH})_2$ and H_2CO_3 . By maintaining a pH between 6 and 9 in the resulting solution, subsequent hydroxide reactions with CO_2 would primarily produce dissolved calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, and for each mole of CaCO_3 split, there can be a net capture of up to 1 mole of CO_2 . The resulting dissolved $\text{Ca}(\text{HCO}_3)_2$ can be diluted and stored in the ocean, or in reservoirs on land or underground. This is one of the many proposed remedies that look perfectly feasible on the bench scale, but their applicability on the gigantic oceanic scale that, too, without causing negative fall-outs, is so uncertain that they generate little hope.

In summary, the only feasible strategy to reduce the scale of future changes to the chemistry and acidity of the oceans appears to be the prevention of further accumulation of CO_2 in the atmosphere.

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